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Preliminary Environmental Assessment of Coal-Fired Fluidized-Bed Combustion Systems

GCA Corp, Bedford, Mass GCA Technology Div

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Industrial Environmental Research Lab, Research Triangle Park, N C

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PRELIMINARY ENVIRONMENTAL ASSESSMENT OF COAL-FIRED FLUIDIZED-BED COMBUSTION SYSTEMS

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by

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ABSTRACT

This report provides a preliminary evaluation of the potential pollutants which could be generated in coal-fired fluidized bed combustion processes. Because SO_2 and NO_x formation have already received considerable attention from a number of investigators, the primary emphasis here is on the so-called "other" pollutants – namely, trace elements, organic compounds, inorganic compounds (other than SO_2 and NO_x) and particulates.

Using available bench scale or pilot plant data and/or simple thermodynamics and empirical correlations with data from other combustion systems, order of magnitude estimates have been made of the concentrations of various elements and compounds in either the flue gas, the solid waste, or the water discharge.

The results suggest that, in general, no special environmental problems should result from coal-fired fluidized bed combustion. But the results also indicate that better data are required in several areas, particularly with regard to particle size distributions, possible organic compounds, and the fate of elements such as Se, As, U, Pb, Cd, Ni, Cl, Be, F and their compounds.

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SECTION I

SUMMARY

GENERAL COMMENTS

This report provides a preliminary evaluation of the potential pollutants which could be generated in coal-fired fluidized bed combustion processes. Because SO_2 and NO_x formation in fluidized bed combustion have received considerable attention from a number of investigators, the primary emphasis here is on the so-called "other" pollutants - namely, organic compounds, inorganic compounds (other than SO_2 and NO_x), trace elements and particulates. The major purpose in a sense has been to serve as a 'devil's advocate" with respect to pollutant generation. The aim is to focus attention on potential environmental problems as early in the development cycle as possible. Accordingly, conclusions are often based on limited data; in some cases, no data are available and one must rely on scientific and engineering estimates. The results are intended primarily to stimulate interest in potential problem areas and to assist in the design and planning of future experimental programs.

Based on data from bench scale reactors, fluidized bed combustion offers significant potential for reducing atmospheric trace element emissions in comparison with conventional coal combustion systems, but data on trace element emissions from larger fluidized bed pilot plants are still lacking. Also lacking are data with respect to trace element composition as a function of particle size. Based on "worst case" analyses with bituminous and lignite coal as feed materials, elements whose emission pathways warrant further attention are: Be, As, U, Pb, V, Cl, and F.

Limited experimental data on particulate emissions from atmospheric pressure bench scale and pilot plant operations indicate that control devices such as cyclones, fabric filters or electrostatic precipitators should be able to control emissions to a level similar to that attained in conventional combustion systems. However, the compatibility of particulate control devices with full-scale fluidized bed boilers has not yet been tested; the need for experiments in this area is very important. Controlling particulates in pressurized fluidized bed is a difficult matter. Pilot plant experiments indicate the use of two stage cyclones will not meet current New Source Performance Standards. As yet, no satisfactory third stage device which can operate at high temperature and pressure has been demonstrated.

There is virtually no experimental information available concerning potential organic pollutants which could form in coal-fired fluidized bed combustion. An evaluation based on chemical engineering experience and simple thermodynamic considerations indicates no special problems should occur from gaseous organic pollutants; however, experimental verification of estimated emission rates should receive high priority.

The following generic classes of "potential" pollutants have been considered in this report:

- Acids and Acid Anhydrides

  - Organic Acids - Compounds such as carboxylic acids, dicarboxylic acids, and sulfonic acids could conceivably form from incomplete combustion of hydrocarbons; however, at the temperatures involved (~850°C), compounds of this type should quickly decompose to form small hydrocarbons and CO_2.

  - Inorganic Acids - The predominant inorganic acids should be HCl and HF. Sulfuric, sulfurous, nitric and nitrous acid should not form until the flue gas has cooled to temperatures less than 260°C.

- Carbon Compounds

  The major carbon compounds, as expected, will be CO_2 and CO. Soot (solid carbon) could be a problem since it would be emitted as small particles (< 0.1 μm) which could pass through most particulate control devices. Calcium and magnesium carbides could also form in small quantities in the ash formed in the combustor, the carbon burn-up cell or the regenerator. After ash disposal, these compounds could release acetylene upon contact with water. The quantities generated, however, should pose no special problems.

- Halogen Compounds

  Halogens should be emitted primarily as HX (where X = F, Cl, Br). Experience in coal combustion chemistry indicates that the presence of chlorine in coal enhances condensation reactions via elimination of HCl; hence, species such as chlorinated hydrocarbons are not favored. Furthermore most chlorinated aliphatics are unstable at the temperatures prevailing in the combustor.

- Hydrocarbons

  Long chain aliphatics and cyclic hydrocarbons should decompose within the bed to form H_2 and smaller hydrocarbons. Some of these smaller hydrocarbons could recombine to form polycyclic species such as pyrene, anthracene, etc. Hydrocarbon concentrations are strongly dependent on the amount of excess air. With excess air levels of about 20 percent, total hydrocarbon levels (measured as methane) of less than 100 ppm are attainable. Based on a comparison with data from conventional combustion systems, 1 ppb of benzo(a)pyrene (or similar compounds) could be present in fluidized bed combustion. With excess air levels of 10 percent, benzo(a)pyrene could reach 10 ppb.

- Nitrogen Compounds

  The predominant nitrogen compound should be NO. Trace amounts (< 1 ppm) of HCN, $(CN)_2$ and isocyanates may be present. Species such as amines, pyridine, pyrroles, and nitrosamines, which could form as combustion intermediates, should quickly decompose within the bed to form hydrocarbons, NO and HCN.

- Oxygen Compounds

  Oxygenated hydrocarbons such as furans, ethers, esters, aldehydes, etc. could form as combustion intermediates. These species, however, are unstable at temperatures on the order of 850°C, and they should decompose before escaping from the bed. Ozone, if formed, would also decompose at these temperatures.

- Particulates

  As mentioned earlier, although there are only very limited data available on particulate concentrations and particle size distributions, it seems that no special problems should result from particulate loadings, provided the conventional process cyclones and a control device such as an electrostatic precipitator or a fabric filter are used. The actual performance of these devices on full-scale fluidized bed boilers, however, has not yet been tested.

- Radioactive Isotopes

  Based on a "worst case" analysis with lignite coal, uranium could be emitted at significant levels, but the radioactive isotopes of uranium as well as those of other radioactive elements should not be present in high enough quantities to cause concern.

- Sulfur Compounds

  SO_2 and SO_3 will be the major sulfur compounds formed. The presence of limestone in the bed, however, should keep these emissions below present emission standards. COS could form in trace quantities (~1 ppm). Compounds such as thiophenes or mercaptans, if formed as combustion intermediates, will decompose to hydrocarbons and H_2S; the H_2S will then be oxidized to form SO_2.

- Trace Elements

  Data should be acquired with respect to the fate of trace elements such as Be, As, Pb, V, Ni and Cl. Also needed are data with respect to chemical composition as a function of particle size. For the most part, the other trace elements commonly encountered in coal combustion are captured in the coarse solids and remain in the bed. The high pH of the bed material is advantageous in that it tends to retard the leaching of the heavier metals.

ESTIMATED CONCENTRATION RANGES OF POTENTIAL POLLUTANTS FROM COAL-FIRED FLUIDIZED BED COMBUSTION

Using available data and/or simple thermodynamics and empirical correlations, estimates have been made of the concentrations of various elements and compounds in either the flue gas or the solid waste. In some cases, these estimates are based on simple and tenuous assumptions; but, in general, they should be good to within an order of magnitude. The main purpose of estimates such as these is to help define experiments which can be used to test the environmental acceptability of fluidised bed combustion.

Flue Gas

One hundred parts per million: (100 ppm)	CH_4, CO, SO_2, NO
Ten parts per million: (10 ppm)	SO_3, C_2H_4, C_2H_6, HCl
One part per million: (1 ppm)	HF, HCN, NH_3, $(CN)_2$, COS, H_2S, H_2SO_4, HNO_3, Elemental Vapors, As, Pb, Hg, Br, Cr, Ni, Se, Cd, U, Be, Na
One part per billion: (1 ppb)	Diolefins, Aromatic Hydrocarbons, Phenols, Azoarenes
One-tenth part per billion: (0.1 ppb)	Carboxylic Acids, Sulfonic Acids, Alkynes, Cyclic Hydrocarbons, Amines, Pyridines, Pyrroles, Furans, Ethers, Esters, Epoxides, Alcohols, Ozone, Aldehydes, Ketones, Thiophenes, Mercaptans, Chlorinated Hydrocarbons

Solid Waste

0.1 to 1 percent	Al, Ca, Fe, K, Mg, Si, Ti, Cu, Na

Ten parts per million (10 ppm)	Cu, Ni, Co, Pb, As, U
One part per million (1 ppm)	Zn, V, F, Br, Cl
One part per billion (1 ppb)	Ba, Ce, Mn, Rb, Sc, Sr, Cd, Sb, Sn, Be
One-tenth part per billion: (0.1 ppb)	Au, Hf, La, Sm, Ta, Th

SECTION II

INTRODUCTION

The overall technical objective of this project is to provide a preliminary evaluation of the potential pollutants which could be generated in all variations of coal-fired fluidized bed combustion processes. In performing a preliminary environmental assessment, one's major role in a sense is to serve as a "devil's advocate" with respect to pollutant generation. The aim is to focus attention on potential environmental problems as early in the development cycle as possible. This provides maximum lead time to gather the technical data on which decisions regarding control technology or process modifications (should they be needed) can be based. This particular project was divided into three phases.

The first phase was to provide a review of fluidized bed combustion technology and to identify conceivable pollutants. An overview of fluidized bed combustion systems appears in Section III. The identification of conceivable pollutants was based on the materials involved (coal, bed material, etc.) and pertinent process parameters (temperature, pressure, etc.); a list was made of possible pollutants which could be emitted from coal-fired fluidized bed combustion processes. This list, which is provided in the Appendix, served as the focal point of the second phase, which consisted of an engineering and scientific evaluation to determine at what concentration levels the pollutants identified in phase I could exist in the various effluent streams (air, water, solid waste) of a fluidized bed combustion system. The methods used to estimate the various pollutant levels for the major unit operations of a fluidized bed

combustion system are described in Section IV which forms the main body of the report. The primary emphasis was on trace elements, inorganic compounds, organic compounds and particulates; SO_2 and NO_x have already received considerable attention. This evaluation included calculations or extrapolations based on available laboratory or pilot plant data. In cases where data were lacking, simple kinetic or thermodynamic estimates were used. No emission measurements were made as part of this program.

The third phase, which is described in Section VI, involved the providing of suggestions for appropriate control measures to reduce any emissions which may exist at undesirably high levels.

This project was part of EPA's Program for Environmental Characterization of Fluidized Bed Combustion Systems. It is the first step in a long-range environmental assessment program being carried out by a number of contractors which will include: more detailed process stream information, a comprehensive analysis of emissions, control technology assessment and environmental impact analysis. The overall program strategy has been recently described.[1]

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1. Henschel, D. B. The U.S. Environmental Protection Agency Program For Environmental Characterization of Fluidized Bed Combustion Systems. (Presented at the Fourth International Conference on Fluidized Bed Combustion. Sponsored by U.S. Energy Research and Development Administration. McLean, Virginia. December 1975.)

SECTION III

OVERVIEW OF FLUIDIZED BED COMBUSTION SYSTEMS

A fluidized bed boiler can be simplistically depicted as an enclosed cavity containing boiler tubes and a bed of granular solids, to which fuel is added. As shown in Figure 1, the solids are supported on a grid at the bottom of the boiler through which combustion air is passed at high velocities, typically 2 to 5 feet per second. The solids are held in suspension by the upward flow of the air and a quasi-fluid is created which contains many properties of a liquid. The most important liquidlike property to the boiler designer is the fact that the bed material is exceptionally well mixed and flows throughout the system without mechanical agitation.

Fluidized bed coal combustion systems for the production of steam and/or electricity have several advantages over conventional combustion systems.[1,2] Capital and operating costs should be lower for the following reasons:

- High heat transfer coefficients and volumetric heat release rates will reduce the boiler size by 1/3 to 2/3 or more compared to a conventional unit.[1]
- Capital costs will be reduced due to the size reduction and the potential for shop fabrication instead of field construction.[1,2,3]
- First generation plants[1,2,3,4,5] should achieve fuel-to-electricity efficiencies comparable to the best conventional systems (36 to 38 percent)[1-5] while second generation plants may achieve higher efficiencies of 40 to 47 percent.[2] The higher efficiencies will be achieved by operating at higher steam temperature and pressure than is possible with a conventional system.

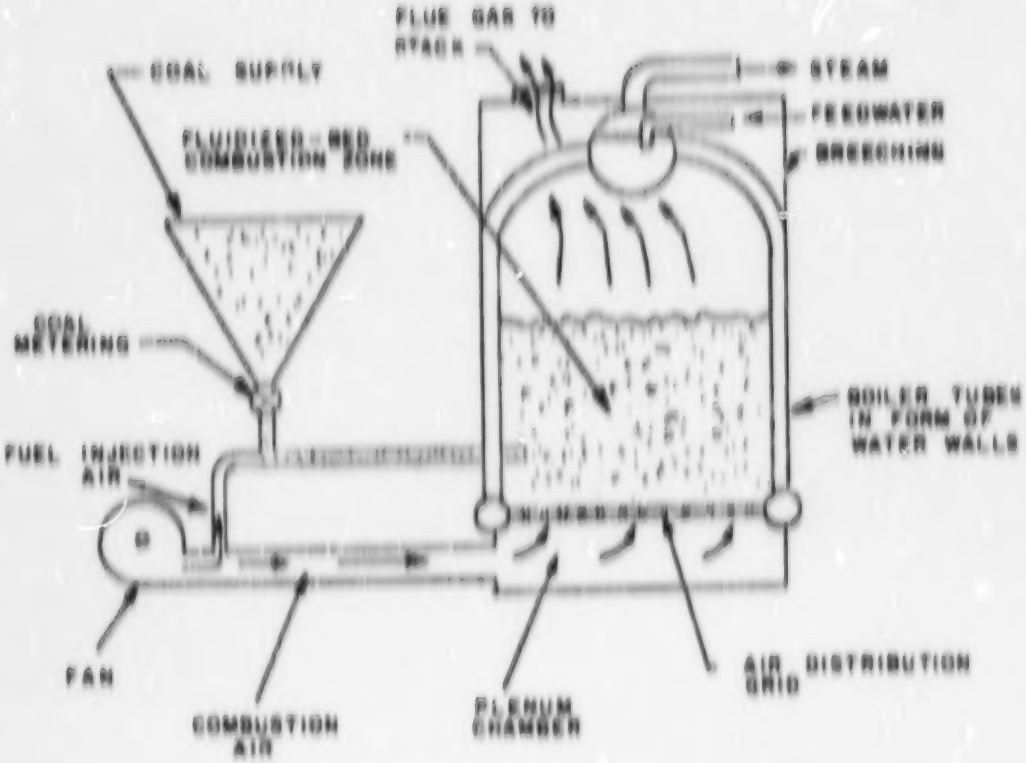

Figure 1. Schematic of fluidized bed boiler

Flue gas emissions of SO_2 and NO_x will be reduced without the use of auxiliary control equipment. A limestone bed will collect the SO_2 while the NO_x emissions will be low due to the inherent ability of fluidized bed combustors to achieve low NO_x emissions. The mechanism for reducing NO_x emissions is not completely understood. It involves low thermal fixation of atmospheric nitrogen as well as low conversion of fuel nitrogen to NO_x. Cooling requirements will be reduced for those fluidized bed systems that use gas turbines to extract part of the energy.

Potential problem areas include environmental impacts of limestone regeneration and/or solid reuse disposal and unknown flue gas emissions. Potential pollutants which could form in FBC flue gases but have not yet been measured are discussed in depth in later sections of this report.

TYPES OF FLUIDIZED BED COMBUSTION SYSTEMS

A fluidized bed combustion system is defined by a combustor, an energy use or conversion cycle, and a spent stone regeneration or disposal method, as well as numerous auxiliary systems. Some major options regarding combustor design conditions include operation of the bed at atmospheric versus elevated pressure and the presence or absence of heat transfer surfaces in the bed. Energy may be generated as process steam or converted to electric energy through steam turbines, gas turbines, and combined systems. Stone processing options include: (1) no processing (once-through operation) and (2) one-step or two-step regeneration followed by sulfur recovery, sulfuric acid recovery, or SO_2 scrubbing. Figure 2 presents some of the most probable options for selected variables in a complete fluidized bed combustion system.

Three basic combustion types can be defined by the operating pressure and excess air. These are atmospheric combustion, pressurized combustion (15 to 25 percent excess air) and adiabatic combustion (pressurized and 100 percent excess air). The energy output from the atmospheric combustor will be steam from tubes in the bed for process use or conversion to

electricity. Pressurised systems (both normal excess air and adiabatic) will produce electricity through steam and gas turbines. The normal excess air pressurised system energy output will be 80 percent through a steam turbine (driven by steam generated in tubes in the bed) and 20 percent through a flue gas turbine. In the adiabatic system, no heat transfer tubes will be in the bed and the total amount of heat will be absorbed by the large amount of excess air. The energy will be extracted from the flue gas and converted to electricity by the flue gas turbines (80 percent) followed by a waste heat boiler/steam turbine combination (20 percent of energy output). Without the waste heat boiler, the fuel-to-electricity efficiency of the adiabatic system would be low (35 percent).[6] Even with the waste heat boiler, the efficiency will probably be lower than the normal excess air pressurised system.[7]

The atmospheric pressure combustion system has been simpler to develop, should be easier to operate and is in the most advanced stage of development compared to other fluidised bed systems. Two reasons for the relative ease of operation and more advanced development have been the lower pressure and and lack of need for flue gas turbines. Pope, Evans and Robbins, Inc.[8,9] have developed a process and are building a system under an Energy Research and Development Administration contract. Under a subcontract, Foster Wheeler is assisting with the detailed design and construction of the demonstration plant. The demonstration plant will have a fuel input capacity of 375×10^6 Btu/hr or 28,800 lb/hr of coal at the projected heat content of 13,000 Btu/lb (30 MW). The size of the unit will be similar to an industrial boiler, thus serving as a demonstration for industrial utilisation and a scale-up step toward a utility size unit. Construction of the demonstration plant is progressing with shakedown scheduled for completion in 1977. Pope recently told a Congressional subcommittee that commercial use of fluidised bed combustion could be possible by 1979.[10] ERDA and the Electric Power Research Institute (EPRI) are considering the design and construction of a 200 MW boiler as the next step in a combined development/demonstration program.[10]

The pressurized fluidized bed combustion system operating at normal excess air appears to be an economically attractive system compared to conventional coal-fired utility boilers and to atmospheric pressure systems.[5,7] One reason is the small size and lower capital cost. The pressurized combustion concepts have only been evaluated as a utility application because a percentage of the energy must be recovered from the flue gas as mechanical or electrical energy and because the system is more complex. In addition, the potential advantages of higher steam temperature and pressure (improved fuel-to-electricity efficiency) are only applicable to utility systems.

High temperature gas cleaning to prevent turbine blade erosion is one area of technical investigation.[5,11]

The National Coal Board of England has operated a 2-foot by 3-foot, five atmosphere pressurized combustor with a heat input of 4.0 to 6.3 × 10^6 Btu/hr for at least the past 5 years.[12] Exxon began operation of a 13.5-inch diameter 10 atm "miniplant" with a capacity of 6.3 × 10^6 Btu/hr in 1975.[13] ERDA has recently awarded a contract to Curtiss-Wright Inc. for the development of a 10 MW unit which is a cross between a steam-tube and adiabatic design. The International Energy Agency is also planning a 30 MW unit in England.

Combustion Power Company is primarily responsible for development of the adiabatic fluidized bed combustion concept; coal combustion work at Combustion Power is funded by ERDA. The adiabatic combustor appears to have several disadvantages, including the much larger volumes of gas that must be handled at 300 percent excess air instead of 15 to 25 percent. In addition, preliminary estimates indicate a lower fuel-to-electricity efficiency.[7] Handling large volumes of gas and lack of boiler tubes in the bed appear to negate two potential advantages of fluidized bed combustion, mainly small size and high heat transfer rates. Possible advantages of the system are complete combustion without a carbon burn-up cell, no boiler tube erosion and the ability to burn low grade fuels including

refuse. Combustion Power Company has operated a 7-foot diameter process development unit at about 25 × 10^6 Btu/hr heat input and is testing turbine performance and life.[5]

Although a commercial atmospheric pressure and possibly a pressurized fluidized bed combustion system should be in operation by the early 1980's, they will not be widely used in the utility industry until the late 1980's. One reason is the long lead time of 5 or more years involved between planning and operating an electric power plant.

POTENTIAL EFFLUENT STREAMS FROM FLUIDIZED BED COMBUSTION

In a complete fluidized bed combustion system there are many potential effluent streams including air emissions, liquid wastes and solid wastes. Figure 3 is a schematic diagram of a complete atmospheric pressure fluidized bed combustion system. Estimates of the numbered flows normalized to a coal feed of 1 pound per hour are presented in Table 1. (Flow diagrams for the stone regeneration system will be presented later.) Many of the effluent streams will be similar to a conventional coal-fired steam power plant as described in reference 15. A few minor effluent streams, such as preoperational and operational boiler water side cleaning wastes and boiler and air preheater fireside cleaning wastes, have not been included. Figure 3 is based primarily on the Pope, Evans and Robbins (PER) system[8] with emission points, cooling tower systems, and water treatment systems added by GCA. (Details on the emission streams are presented in later sections of this report.)

Based on the overall flow of materials depicted in Figure 3, the fluidized bed combustion system can be categorized into the following major unit operations:

- Fluidized Bed Combustion
- Limestone Regeneration
- Solid Waste Disposal

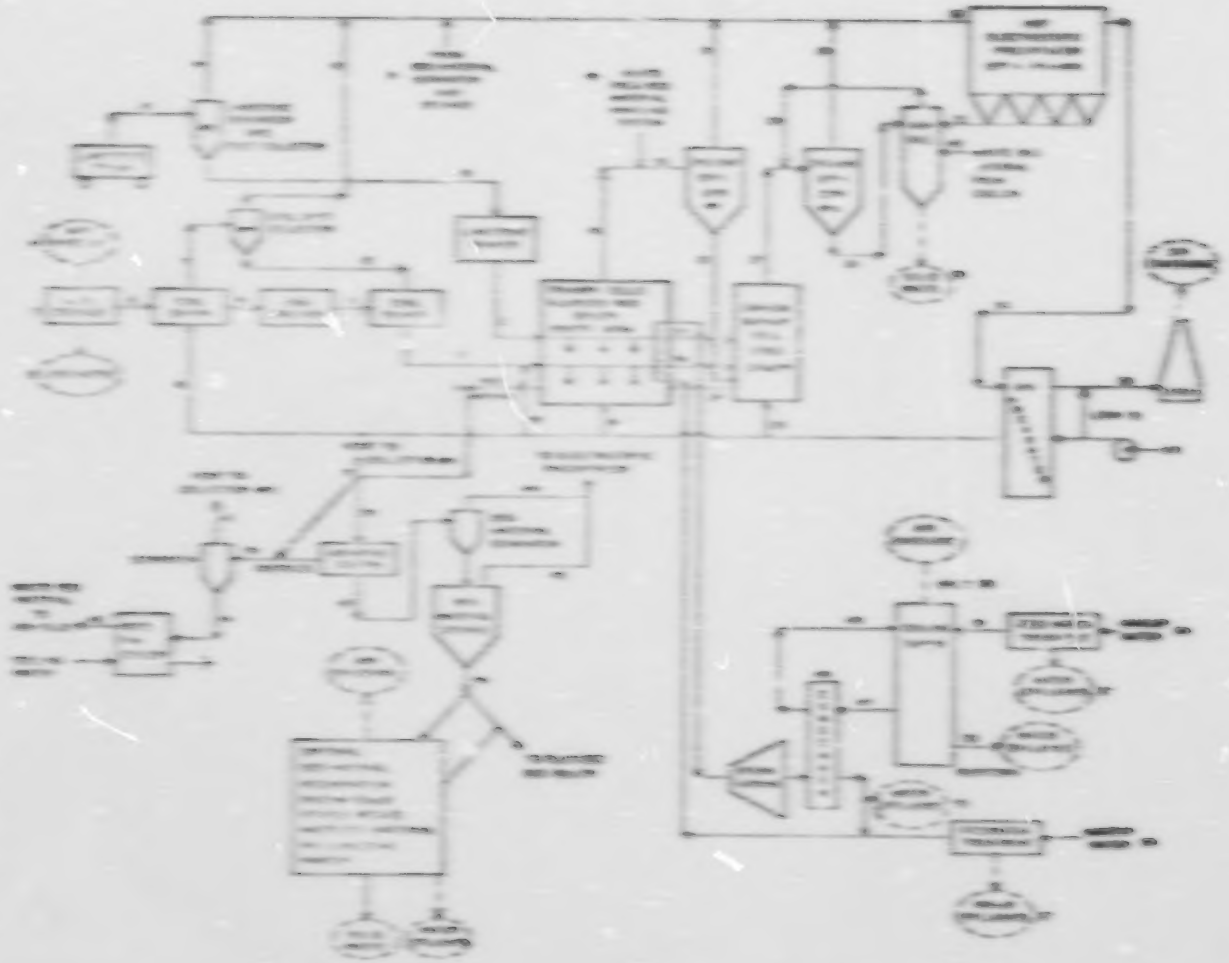

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Figure 1. Schematic diagram of an atmospheric pressure fluidized bed combustion system (reference 8 was a basic data source; CCA added emission points, cooling tower, and water treatment system)

Table 1. ATMOSPHERIC PRESSURE FLUIDIZED BED COMBUSTION SYSTEM MATERIAL FLOWS AND CHARACTERISTICS[a]

Material flows	Solid				Gas	Liquid	Temp., °F
	Total	Carbon	Ash	Sulfur			
1. Coal feed to beds[b]	1.0000	0.7159	0.085	0.043	–	–	60
2. Limestone feed to beds[c]	0.1709				–	–	60
3. Coal storage[d]	1960	1190	160	84	–	–	60
4. Air emissions from coal storage	0.0006	0.0005	0.0004	0.0004	–[e]	–	60
5. Coal pile drainage	0.0004			0.[illegible]003–0.0004	–	0.079	60
6. Coal feed to dryer	1.0–1.1	0.712	0.085	0.043	–	–	60
7. Air emissions from coal dryer before primary control	0.01	0.0071	0.00085	0.00043	1.2	–	160
8. Hot air to coal dryer	–	–	–	–	1.1	–	600
9. Coal feed to crusher	0.993	0.707	0.079	0.040	–	–	160
10. Air emissions from coal dryer after primary control but before ESP	0.003	0.002	0.0001+	0.00013	1.2	–	160
11. Coal feed from crusher	0.963	0.707	0.079	0.040	–	–	160
12. Solids from coal dryer primary control	0.007	0.005	0.0004	0.003	–	–	160
13. Limestone supply from truck	0.1712				0.005	–	60
14. Air emissions from lime-storm separator	0.005				0.005	–	60
15. Limestone to storage hopper	0.1709				–	–	60
16. Flue gas from primary fluidized bed combustion cells (FBC)	0.7941	0.0401			11.24		730
17. Bed material from FBC (ave)	2.28					–	1400
18. FBC combustion air[f]	–	–	–	–	9.95	–	600

Table 1 (continued). ATMOSPHERIC PRESSURE FLUIDIZED BED COMBUSTION SYSTEM MATERIAL FLOWS AND CHARACTERISTICS[a]

Material flows	Solid				Gas	Liquid	Temp., °F
	Total	Carbon	Ash	Sulfur			
29. Vents from bed material handling system	0.002				0.069	-	1400
30. Materia: to cyclone no. 1 (sum of 26 + 29)	0.2961	0.0983			11.33	-	730
31. Air emissions after cyclone no. 1	0.0146	0.00049			11.33	-	730
32. Cyclone no. 1 bottoms (solids) to carbon burn-up cell (CBC)	0.2765	0.09642			-	-	730
33. Limestone to CBC	0.0437				-	-	ar
34. Coal to CBC	0	0	0	0	0	0	-
35. Combustion air to CBC[b]	-	-	-	-	1.26	-	600
36. CBC bed material to FBC	0.3247				-	-	2000
37. Air emissions from CBC before primary collector (cyclone no. 2)	0.3579	0.0047			1.267	-	730
38. Air emissions from ash silo to cyclone no. 2							
39. Air emissions from cyclone no. 2 to ESP	0.0198	0.0010			1.267	-	730
40. Bottom material from cyclone no. 2 to ash silo	0.1661	0.0087			-	-	730
41. Vents fr:a bed material separator and storage to ESP	0.003				0.104		1400
42. Inlet to electrostatic precipitator (sum of 18 + 34 + 21 + 39 + 41)	0.0397	0.001248			14.002	-	730

Table 1 (continued). ATMOSPHERIC PRESSURE FLUIDIZED BED COMBUSTION SYSTEM MATERIAL FLOWS AND CHARACTERISTICS[a]

Material flows	Solids				Gas	Liquid	Temp., °F
	Total	Carbon	Ash	Sulfur			
33. Material collected by electrostatic precipitator (ESP = 0.96 × min)	0.9361				–	–	730
34. Outlet of ESP	0.0026				14.882		730
35. Maximum gas leak	–	–	–	–	1.66	–	105
36. Air emissions from stack (sum of 34 + 35)	0.0026				15.542	–	270
37. Vent from screens and bed material transfer	0.008				0.035	–	1400
38. Bed material to screens	2.57					–	1400
39. Waste bed material	2.1435 (0.694 max)					–	1400
40. Vent from waste bed material separator before cyclone cooler	0.008				1.035		1400
41. Waste bed material to cyclone cooler	0.1445				–	–	1400
42. Cooled waste bed material to ash silo	0.1445				–	–	700
43. Fine bed material from vibration screens	2.43				–	–	1400
44. Air emissions from bed material separator to ESP	0.0026				0.097	–	1400
45. Air emissions from bed material storage to ESP	0.0002				0.0069	–	1400
46. Bed material from storage to FBC	2.43				–	–	1400

Table 1 (continued). ATMOSPHERIC PRESSURE FLUIDIZED BED COMBUSTION SYSTEM MATERIAL FLOWS AND CHARACTERISTICS[a]

Material flows	Solid				Gas	Liquid	Temp., °F
	Total	Carbon	Ash	Sulfur			
47. Cooling water to condenser		-	-	-	-	490	85
48. Cooling requirement	-	-	-	-	-	-	(5800 Btu)
49. Cooling water from condenser						490	
50. Cooling tower drift		-	-	-	-	0.02 (0.01-0.05)	
51. Cooling tower feed water (sum of drift (50) + blowdown (52) + evaporation		-	-	-	-	6.42	
52. Cooling tower blowdown		-	-	-	-	1.3	85
53. Cooling tower water treatment effluent		-	-	-	-	0.04	
54. Total makeup water requirements for cooling tower		-	-	-	-	7.06	
55. Boiler water blowdown							
56. Boiler water makeup requirement							
57. Boiler feed water treatment wastes							
58. Solid waste from ash silo (sum of 30 + 33 + 42)	0.3917				-	-	730
59. FBC combustion air fed with coal[b]	-	-	-	-	0.6	-	730

Table 1 (continued). ATMOSPHERIC PRESSURE FLUIDIZED BED COMBUSTION SYSTEM MATERIAL FLOWS AND CHARACTERISTICS[a]

[a]Based on Figure 1, all flows are pound of material per pound of coal. The design of a 30-MW electrical output requires 74,800 pounds of coal per hour.

[b]Coal, Pittsburgh Seam No. 6, HHV = 13,300 Btu/lb.

Coal		Ash		
Species	Weight %	Species	Weight %	lb/lb coal
C	71.30	SiO_2	45.30	0.0395
H_2	5.07	Fe_2O_3	27.30	0.0252
O_2	6.35	Al_2O_3	21.20	0.0160
N_2	1.30	CaO	1.40	0.0016
S	4.30	K$_2$O	1.80	0.0015
H_2O	3.30	TiO_2	1.00	0.0009
Ash	8.50	MgO	0.60	0.0005
		Na_2O	0.20	0.0002
		P_2O_5	0.10	0.0001
		Misc.	0.60	0.0005
	100.30		100.00	0.085

Table 1 (continued). ATMOSPHERIC PRESSURE FLUIDIZED BED COMBUSTION SYSTEM MATERIAL FLOWS AND CHARACTERISTICS[a]

[c]Limestone, BCR 1359 assumed, Ca:S = 2:1.

Species	Weight %	lb/lb fuel
CaO	55.52	0.1584
CO_2	40.58	0.1158
SiO_2	0.50	0.0014
MgO	0.30	0.0008
Fe_2O_3	0.10	0.0003
Fuel	3.00	0.0041
	100.00	0.2710

[d]Storage capacity (not a material flow).

[e]Carbon monoxide and hydrocarbons from spontaneous combustion. Amount unknown.

[f]Eighteen (18) percent excess air.

[g]Twenty-five (25) percent excess air.

- Coal Storage and Handling
- Coal Drying
- Cooling Operations

The latter operations, coal storage, coal drying and cooling will be similar for all coal combustion systems. The total cooling required, however, will vary with the energy feed to the steam turbine and the efficiency of the turbine. In most cases, cooling equivalent to about 60 percent of the energy input to the steam turbine will be required. Effluent Guidelines and Standards for Steam Electric Power Generation[15] will require recirculative cooling for almost all new plants. A utility will maintain a coal supply of 90 days while industry commonly maintains a supply of 30 days.[15] Wind erosion and handling cause a minor amount of particulate emissions. Leachates from coal storage can be a more serious problem and, as such, are regulated,[16] and control measures are applied. Particulates are emitted from many coal drying operations, but they can be controlled by conventional equipment.

Water treatment is another conventional unit operation. Make-up cooling water is commonly treated by coagulation and clarification with aluminum and iron salts or lime. Polyelectrolytes are used to increase coagulation and sedimentation rates. In some cases, more sophisticated water treatment methods may be needed, depending on the water supply. Waste streams generated by cooling tower make-up water treatment are generally just water streams containing higher concentrations of impurities in the feed water. Even with recirculative cooling, large amounts of make-up water are needed and supply can be a problem.

There are many solids transfer operations involved in operating a fluidized bed combustion system. Conventional practice is to use cyclones for initial solids separation in pneumatic transfer systems with fabric filters as secondary collectors. In the design of the PFBC system, material regenerators and transfer systems will use cyclones vented to the main high efficiency electrostatic precipitator as shown in Figure 3.

The PER system is slightly unusual in that all solid waste products are transferred dry. Wet sluicing is the most common practice at conventional plants, and ash slurring water discharge can be a major water pollution problem.

No significant emissions will occur from coal crushing. In all fluidized bed systems coal will be crushed to about one-quarter inch and less. Coal crushing is a common and conventional unit operation, and the equipment as used by electric utilities is entirely self-contained.

The primary focus of this study is the primary fluidized bed combustor, the carbon burn-up cell (if used), and the regeneration system (if used). The fluidized bed combustion process and factors affecting pollutant formation will be discussed in depth in Sections IV and V of this report. These systems will be the most important potential emission sources. Potentially very large amounts of solid waste may be produced if regeneration is not used. At a Ca/S ratio of 2:1, the PER system generates about 0.35 to 0.4 pound of waste per pound of coal burned. This is more than a conventional system and would amount to about 700,000 tons per year at a typical 500 MW plant.

PRINCIPAL DIFFERENCES BETWEEN FLUIDIZED BED COMBUSTION AND CONVENTIONAL COMBUSTION

Many of the differences and similarities between fluidized bed combustion systems and conventional combustion systems have been described in the previous paragraphs. The discussion here focuses mainly on the primary fluidized bed combustor and the carbon burn-up cell. Perhaps the most important difference from the standpoint of pollutant formation is the low combustion temperature in the primary combustor, most typically 1550 to 1650°F (850 to 900°C). Depending on furnace design, conventional systems may operate at temperatures of over 3000°F (1650°C). The lower temperature of fluidized bed combustion contributes to reduced formation of NO_x and improves the limestone bed reaction with the SO_2, but could cause loss

efficient combustion and possibly larger emissions of organics and CO. In most fluidized bed systems, material containing unburned carbon is recycled either to a carbon burn-up cell or back to the main cell. Conventional utility coal combustors operate with less than 1 percent unburned carbon losses at excess air in the range of 15 to 22 percent.[18] The low operating temperature in fluidized bed combustion also may reduce volatilization of trace metals as discussed in later sections.

Excess air in most designs is very similar to conventional systems — 15 to 25 percent. Higher amounts of excess air in conventional systems lead to greater heat losses in the stack gas and lower efficiencies. The 300 percent excess air used in the adiabatic system greatly exceeds the amount used in any conventional system. That high level of excess air is more typical of refuse incinerators.

Other differences in the design of fluidized bed systems are mentioned at appropriate points throughout this report.

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SECTION IV

POTENTIAL POLLUTANTS FROM A COAL-FIRED FLUIDIZED BED COMBUSTOR

INTRODUCTION

As mentioned earlier in section III, the fluidized bed combustion system has been categorized into the major unit operations or activities listed below:

- Fluidized bed combustion
- Limestone regeneration
- Solid waste disposal
- Fuel storage and handling
- Coal drying
- Cooling operations.

Potential pollution problems from each of these operations are discussed here as separate subsections. The major emphasis has been on analyzing the fluidized bed combustion unit -- and to a lesser extent, the limestone regenerator. These are the operations which are unique to a fluidized bed combustion system. In a sense, the solid waste disposal associated with fluidized bed combustion may also be a unique operation in that the leaching properties of the ash may be different than that from conventional systems, but to date, there is relatively little data available in this regard. The environmental hazards which may result from fuel storage, coal drying, and cooling should differ very little from those also encountered in conventional combustion systems.

FLUIDIZED BED COMBUSTION

Since SO_2 and NO_x formation in coal-fired fluidized beds has been extensively investigated by the U.S. Environmental Protection Agency; Exxon; Argonne National Laboratory; Pope, Evans and Robbins, Inc.; Westinghouse; Battelle; and BCURA; among others, the primary interest here was the so-called "other" pollutants -- namely, organic compounds, trace elements, inorganic compounds (other than SO_2 and NO_x); and particulates. Based on available data and/or simple thermodynamics and chemical experience, estimates have been made of the concentrations of various elements and compounds in either the flue gas or the solid waste. In general, the estimates for the trace elements and particulates are probably good to within an order of magnitude, while those for the organic compounds are probably good only to within two orders of magnitude.

Trace Elements

Trace elements and their compounds are of concern because some of these materials can vaporize and exit with the flue gas. Because vaporized trace elements would be in the gas phase, they would not be captured by particle collection devices.

There is also concern about the enrichment of trace elements on fine particles in combustion processes. Studies have indicated that certain elements can concentrate in selected size ranges of particulates.[1-3] For some elements, such as lead and cadmium, these sizes tend to be less than a few microns in diameter. Such small particles are of special environmental concern because they are difficult to remove from the flue gas and, once emitted, they can be readily embedded in the lung.

[1-3] Numbers refer to references at the end of Section IV, page 62.

In addition, trace elements in the solid residue from the process could present a leaching problem. This possibility is discussed in a later subsection on solid waste disposal.

To assess the importance of trace element emissions in coal-fired fluidized bed combustion, a "worst case" analysis approach was used. For both bituminous and lignite coals, ranges for the heat content and the concentration of trace elements were obtained. Assuming that all of the elemental material would exit with the flue gas as either a vapor or a particulate, a "worst case" emission factor was calculated (lbs/10^6 Btu/hr) using the lowest heating value and highest trace element content of the coals. (Calculations to be described later in this section indicated that the trace element contribution from the limestone sorbent is insignificant.) Based on this emission factor, stack gas concentrations were calculated and diluted by a factor of 10^3 to account roughly for dispersion in the atmosphere. These "ambient" concentrations were then compared to industrial hygiene threshold limiting values (TLVS). Although industrial hygiene threshold limiting values cannot be used to assess the absolute environmental impact of pollutants, they do provide a useful framework in which pollutants can be ranked according to their toxicity. Any element whose predicted "worst case" ambient concentration was within a factor of 100 of the industrial threshold limiting value was considered to be potentially harmful. This safety factor of 100 was arbitrarily chosen to account conservatively for the effects of long-term exposure. (Industrial hygiene limits are usually based on exposures to healthy adults over an 8-hour period.) The results of this investigation suggested that the following trace elements could pose potential environmental problems: Be, As, Pb, Cr, V, Cl, U. But again, the results are based on worst case estimates.

The evaluations from this study also suggested that in comparison with a conventional coal combustion unit, fluidized bed combustion (FBC) might reduce some trace element emissions. Therefore, the application of FBC technology could present an attractive alternative for the control of some

trace element emissions. The major parameters in FBC which will tend to mitigate trace element emissions are expected to be:

- Temperature - The range of combustion temperatures in FBC is 700-1000°C, with most units operating between 800-900°C. In conventional combustion, temperatures are of the order of 1650°C. Therefore, many of the trace elements that oxidize, enrich, or vaporize in a conventional system should be less active in a FBC unit.

- Pressure - FBC units can operate at pressures as high as 20 atm. High pressure can raise the melting and boiling points of the trace element compounds and therefore may potentially decrease air emissions. However, no measurements have been undertaken to confirm this particular aspect of FBC technology.

- Coal size - The coal size used in FBC is larger than that used in conventional combustion. Therefore, fine particulate emissions may be reduced.

- Limestone sorbent - Limestone can modify trace element emissions by acting as a sink for certain trace elements (e.g., Fe).

Trace Elements in Coal and Limestone and "Worst Case" Emission Rates - Coal contains, at trace concentrations (~100 ppm or less), virtually all elements below atomic number 92. For this discussion, it has been assumed that the coals to be used predominantly in FBC are lignite and bituminous coal. The ranges of concentrations of trace elements in these coals in terms of lb/10^6 Btu are given in Tables 2 and 3. Included in Tables 2 and 3 are the maximum emission factors calculated from the lowest heating value of the fuel and the highest trace element content. Because it is impossible to deal with all variations in trace element concentration, this "worst case" emission factor will be used to determine which trace elements may be of environmental concern. The concentration range quoted spans 90 percent of the variations found in different seams. Not all trace elements are included in Tables 2 and 3, because composition data are not available for some elements.

Table 2. ESTIMATED TRACE ELEMENT "WORST CASE" EMISSION FACTORS FOR BITUMINOUS COAL[a]

	Average	Minimum	Maximum	"Worst case" emission factor (no emission control)
Heat content, Btu/lb	12,000	10,500	14,500	
Sulfur, lb/10^6 Btu	1.67	0.58	1.75	5.15
Moisture, lb/10^6 Btu	8.33	2.50	15.0	17.15
Nitrogen, lb/10^6 Btu	1.08	0.83	1.33	1.52
Ash, lb/10^6 Btu	11.67	4.17	29.83	31.81
Minor elements, lb/10^6 Btu				
Al	1.57	0.65	7.31	5.92
Ca	0.25	0.10	5.33	6.09
Fe	1.55	0.29	6.62	7.33
Mg	0.06	0.01	0.50	0.57
K	0.16	0.05	0.69	0.79
Si	2.62	0.69	6.66	7.6
Na	0.06	0.01	0.46	0.53
Ti	0.06	0.01	0.62	0.70
Trace elements, Amount = 10^{-3} lb/10^6 Btu				
Sb	0.42			
As	25	2.50	50.00	57.15
Be	81.3	< 33.33	< 150	171.43
Br	2.08	0.50	6.67	7.62
Bi	0.08			
Cd	41.67	3.33	166.67	190.48
Cr	12.5			
Cd	0.33			
Cl	1250.0			
Co	11.67	3.33	41.67	47.62
Cu	3.33	0.42	8.33	9.52
Cu	10.83	2.50	33.33	38.09
F	66.67	8.33	158.33	180.95
Pb	7.50	3.33	11.67	13.33
Mn	41.67	3.33	75.00	85.71
Hg	0.17	0.06	0.42	0.48
Mo	3.33	0.33	7.50	8.57
Ni	11.67	1.67	33.33	38.09
Ne	2.50			
Te	0.25			
Th	0.08			
Sn	0.83			
U	12.50	8.33	66.67	76.19
V	25.00	1.67	58.33	66.67
Zn	6.67	< 0.83	41.67	47.62
Zr	41.67			

[a]Values taken from references 4 through 11.

Table 3. ESTIMATED TRACE ELEMENT "WORST CASE" EMISSION FACTORS FOR LIGNITE[a]

	Average	Minimum	Maximum	"Worst case" emission factor (no emission control)
Heat content, Btu/lb	6,900	6,500	7,500	
Sulfur, lb/10^6 Btu	1.01	0.29	6.35	6.76
Moisture, lb/10^6 Btu	50.72	28.99	57.97	61.69
Nitrogen, lb/10^6 Btu	1.53	0.72	2.17	2.16
Ash, lb/10^6 Btu	14.69	7.25	21.74	23.81
Minor elements, lb/10^6 Btu				
Al	1.15	0.56	3.8	3.28
Ca	3.31	1.85	8.0	8.79
Fe	0.92	0.15	5.17	5.67
Mg	0.76	0.39	1.81	2.0
K	0.08	0.017	0.23	0.26
Cl	1.53	0.61	5.09	5.58
Na	1.61	0.03	4.84	5.21
Ti	0.04			
Trace elements, Amount x 10^{-5} lb/10^6 Btu				
B	0.38			
As	11.59			
Ba	485.79	176.81	434.28	476.19
Be	2.17	0.14	5.80	6.35
Br	0.15			
Cd	173.91	115.94	289.86	317.46
Cr				
Cu	0.29			
Cl	1669.28	72.46	2898.55	3176.80
Co	10.15	5.39	28.99	31.75
Pb	4.35	1.01	10.1	11.1
Hg	4.34	4.35	21.19	25.58
F	86.96			
Mn	10.15			
Ni	55.07	43.48	66.67	73.02
Se	0.16	0.10	0.13	0.15
Ag	2.58	0.15	5.93	5.59
Sr	10.75	7.17	21.74	23.81
Sn	1.88			
Zn	0.16			
Th	0.14			
Sb	1.3	0.13	8.12	8.88
U	211.39	72.46	347.83	380.95
V	23.19	7.25	43.48	47.62
Zn	17.39	0		
Zr	14.49			

[a]Values taken from references 4 through 11.

The use of limestone or dolomite also adds to the trace element loadings in FBC. However, there are very few analyses available of trace elements contained in the sorbents used in FBC. Table 4 contains data for representative types of dolomite and limestone. Also given in Table 4 is the average trace element content of the fuels. The data show that the trace element concentration of limestone is generally equal to or less than that of the coal feed. The mole ratio Ca:S for most FBC processes will be about 2. Because the coal sulfur content will be approximately 3 percent by weight, one is dealing with weight ratios of coal to limestone on the order of 11 to 1. Therefore, trace element loadings from the limestone sorbent should be small compared to the fuel. Furthermore, because trace elements in the sorbent are contained in a limestone matrix as the fairly unreactive oxide or carbonate, they will probably have much lower emission factors than the more volatile forms of trace elements (such as sulfides) encountered in coal.

Geochemical Classification of Elements in Coal - There have been very few studies performed of trace element emissions from FBC of coal. Therefore, to estimate these emissions, a comparison with trace element behavior in conventional combustion is useful. The primary concern is to identify which trace elements will be emitted as vapors and which will be enriched on small particulates. One can use as a basis for these predictions a geochemical classification of elements.[12] This classification scheme has been used successfully in predicting the emissions from the Allen Steam Plant.[3] Element volatilities and enrichment behavior have also been determined on the basis of elemental or oxide boiling points.[3]

In the geochemical scheme, trace elements in coal are separated into four classes: I. lithophile, II. chalcophile, III. volatile elements, and IV. unclassed elements exhibiting the properties of either Class I or II. Trace elements in each class are listed in Table 5.

Table 4. TYPICAL VALUES OF TRACE ELEMENTS IN LIMESTONE AND COAL (ppm)

Element	Argonne dolomite[a]	Tymochtee dolomite[b]	Limestone[c]	Lignite[d]	Average or typical bituminous[d]
As	1.9[b]	0.366 ± 0.17	< 6	8	10
Ba	5[b]		30-100	200	100
Be	2[b]		< 2	1.5	2.5
Br	2[b]	0.75 ± 1.4	< 0.3		15
Cd	15[b]		< 0.3	0.2	0.5
Ce	0.6[b]		< 3		
Co		1.03 ± 0.21	< 2	3	5
Cr		5.33 ± 0.85	< 10	7	15
Cs		0.139 ± 0.091	< 0.06		
Dy					
Eu		0.0598 ± 0.013	< 1		
Fe	5.6×10^3 a	3260 ± 650	200-2000	1564	1.86×10^4
Hf					
Hg					0.2
K	4.6×10^3 b	2180 ± 440	100-1000	0.1	
La	3.6[b]		0.3-3	551	1927
Mn	55[b]	42 ± 8.4	6-60	38	50
Na	100[b]	303 ± 61	10-100	1×10^3	481
Ni			< 5	7	14
Rb		12.2 ± 2.5	< 2		
Pb			< 5	7	9
Sb		0.0527 ± 0.015	< 0.3	0.4	0.5
Sc	1.1[b]	0.752 ± 0.19	< 0.3		
Se			< 1	1.3	1
Sm		0.656 ± 0.13	< 1		
Sr		130 ± 28	100-1000		
Ta					
Te			< 0.3	0.11	0.3
Th		2.81 ± 0.61	< 0.2		
Ti		0.58 ± 0.12		< 0.1	0.1
Yb					
Zn			< 10	12	8
U		2.23 ± 0.45	< 0.5	130	15
V			0.06-0.6	10	30

[a]Reference 11

[b]Reference 14;

[c]Reference 15;

[d]References 4 through 11;

Table 5. THE SEPARATION OF ELEMENTS IN THE GEOCHEMICAL CLASSIFICATION SCHEME[17]

Class I	Class II	Class III	Class IV
Al Nb	As	Hg	Cr
Ba Rb	Cd	Cl	Cs
Ce Sc	Cu	Br	Na
Co Si	Ga	F	Ni
Eu Sm	Pb		U
Fe Sr	Sb		V
Hf Ta	Se		
K Th	Zn		
La Ti			
Mg			

Trace elements listed in Class I are lithophiles and are associated with aluminosilicate minerals in coal. As such, they are high boiling compounds and do not decompose on combustion. They usually melt and coalesce to form the fly ash and slag. Elements in this class are not enriched during combustion.

Class II elements are generally present in coal as sulfides. These sulfides themselves may be fairly volatile or, upon combustion, the sulfides decompose and the elements themselves are produced in the vapor phase. These volatile sulfides or elements can then condense on the extensive surface area presented by particulates thus leading to a surface enrichment. This enrichment is usually most prevalent in the fine particle fraction ($\leq$ 3 μm) of the total particulate loading. Generally, elements could be placed in Class II if:

$$\text{Enrichment factor} = \frac{(x)\ \text{fly ash}}{(x)\ \text{fuel}} > 1$$
$$\text{(EF)}$$

where (x) is the concentration in weight percent.

Class III elements boil below the furnace and flue gas temperatures and can exit from the stack as vapors.

Of the Class IV elements, only Cr and Ni tend to show chalcophile (or volatile) characteristics.

Fate of Trace Elements in FBC - There have been several studies of the behavior of trace elements in FBC. The most complete study has been performed on Argonne National Laboratory's bench scale pressurized combustor.[13,16,17] Trace element studies have also been initiated at Exxon's pressurized bench scale combustor.[14] Table 6 is a comparison of Exxon's and Argonne's results, and the agreement is encouraging.

Table 6. COMPARISON OF EXXON AND ARGONNE DATA ON TRACE ELEMENT RECOVERIES[a]

Element	Recovery, %	
	Exxon	Argonne
As	86	85
Br	no data	18
Fe	80	103
K	75	90
Mn	96	130
Na	88	96
Sc	85	97

[a]Recovery = percentage of element entering combustor that can be accounted for in solids leaving combustor.

Based on their bench scale tests, workers at Argonne as shown in Table 7, have indicated that FBC, compared to conventional combustion, has a propensity for reducing trace element emissions.[17]

Argonne has also performed several experiments to determine the volatility of trace elements during coal ashing. These experiments involve subjecting a previously formed low temperature ash to elemental analysis after exposure to successively higher temperatures.[17] Their results

indicate that Fe, Al, Na, K, Mg, Ca, Ti, Sn, Mn, Ni, Co, Cu, Cr, La, and V all remain in the ash at FBC temperatures which suggests that, if enrichment or volatilisation of these elements does occur, it must result from reactions of compounds in the coal and not the ash. Caution is required, however, in extrapolating these results to larger systems because the heating rates may not be typical of those encountered in commercial combustion systems.

Table 7. PROJECTED ATMOSPHERIC EMISSIONS OF TRACE ELEMENTS FROM CONVENTIONAL AND FLUIDIZED BED COMBUSTORS EXPRESSED AS A PERCENTAGE OF THE ELEMENT ENTERING THE SYSTEM[16]

Element	Conventional combustion[a]	Fluidized bed combustion
Hg	90	80
F	90-100 (estimated)	40
Br	100 (estimated)	65
As	50-60	15
Pb	0-60	0-20
Be	Not available	20-40
Sc	10	0
Cr	0	25
Co	10-20	0-20
Na	20	5
K	30	10
Fe, La, Mn	0	0

[a]Projected from data in the literature on trace element emissions from conventional power plants - see reference 16 for further references.

"Worst Case" Emission Factors - The preceding discussions indicate that elements in Class I should not be enriched or volatilized during FBC or conventional combustion. Therefore, using the "worst case" emission factors (i.e., all of the trace element in the feed is emitted to the

stack as particulate) from Tables 2 and 3 and an assumed collection efficiency of 99 percent for a particulate control device (e.g., an electrostatic precipitator or fabric filter), pollutant loadings at the top of a stack can be calculated for the trace elements in Class I. The results of this calculation are presented in Table 8.

The emission rates in Table 8 have then been divided by 1000 to account for atmospheric dilution. To assess the environmental impact of these estimated ambient concentrations, occupational hygiene threshold limiting values (TLV) are used.[8] As shown in Table 8, these are arbitrarily divided by 100 to provide an environmental index which accounts for long-term exposure. While these cannot be used to assess the absolute environmental impact of pollutants, they do provide a useful framework in which pollutants can be rank ordered according to their degree of toxicity. The minor elements present in coal, with the exception of Na, are all in Class I and therefore are not enriched or vaporized in FBC; hence, it can be concluded that FBC of coal should present no problems for atmospheric trace element emissions of Class I elements.

Trace element emissions for elements in Classes II, III, and IV are more difficult to predict because of their possible volatility which could lead to vapor phase emission which escape through a particulate control device or to enrichment on fine particulates which are less efficiently collected. Table 9, for example, which provides cut-off data on the boiling points of a number of compounds which could either be contained in coal, or formed as combustion intermediates, can be used to provide some insight on the partitioning of elements between the solid (ash) and vapor phase. Table 10 presents "worst case" emission estimates for Class II, III, and IV elements calculated in the same manner as the Class I elements shown earlier in Table 8. Because of the potential volatility of these Class II, III, and

[8] American Conference of Governmental Industrial Hygienists - Threshold Limiting Values.[9]

Table 8. COMPARISON OF ESTIMATED TRACE ELEMENT CONCENTRATIONS (CLASS I ELEMENTS) WITH AN ENVIRONMENTAL INDEX BASED ON THRESHOLD LIMITING VALUES

	A		B		C	D	
	Emission factor after control device (assuming 99% control of particulates)		Estimated ambient concentration (A/1000)		Environmental index (FC/1000)	Ambient concentration/ (D ≥ 1.0 indicates a potential environmental problem)	
Element	Bituminous[a]	Lignite[a]	Bituminous	Lignite		Bituminous	Lignite
Al	11.5	46.11	0.075	0.068	–	–	–
Sb	0.23	0.70	2.3×10^{-4}	7.0×10^{-4}	1×10^{-3}	0.23	0.16
As	89	129	0.089	0.129	0.01	1.0	2.0
Ba	0.06	0.02	6×10^{-5}	2×10^{-5}	–	–	–
Be	0.91	0.01	1×10^{-3}	1×10^{-5}	1×10^{-3}	0.01	0.01
Bo	1.4×10^{-1}	2.8×10^{-5}	1.4×10^{-1}	2.8×10^{-5}	–	–	–
Br	105	84	0.105	0.084	0.13	0.72	0.56
Cd	5.5×10^{-3}	5×10^{-4}	5.5×10^{-3}	5×10^{-4}	0.005	0.01	0.001
Cl	11.6	1.8	11.6×10^{-3}	1.8×10^{-3}	–	–	–
Cr	0.011	0.004	1.1×10^{-5}	4×10^{-6}	–	–	–
Hg	0.5	29.5	0.298	0.72	0.10	0.08	0.1
Mn	0.1	0.1	0.001	0.001	0.01	0.02	0.02
Mo	0.21	0.592	2.1×10^{-4}	2×10^{-5}	–	–	–
Ni	0.03	0.01	3×10^{-5}	1×10^{-5}	–	–	–
Pb	111	86	0.11	0.08	0.1	1.0	1.0
Se	0.001	0.01	1×10^{-6}	1×10^{-5}	0.01	0.0002	0.0005
Sr	0.01	0.66	1×10^{-5}	6.6×10^{-4}	–	–	–
Te	0.0003	–	3×10^{-7}	–	0.01	6×10^{-5}	–
Th	0.0001	0.0002	1×10^{-7}	2×10^{-7}	1×10^{-3}	1×10^{-4}	2×10^{-4}
Ti	10.3	1.5	0.01	0.001	0.1	0.1	0.01

[a]Based on References 4 through 11.

Table 9. BOILING POINTS OF COMPOUNDS OFTEN FOUND IN COAL

Boiling or sublimation points < 1000°C	Boiling or sublimation points > 1000°C
$AlCl_3$	Al_4C_3
Sb_2O_3	Pb_2O_3, Sb_2S_3
As_2S_3, As_2S_2, AsH_3	
$BeCl_2$	BeO
$Cr(CO)_6$	$CrCl_3$
$Co(CO)_6$	$CoCl_2$
CuS	Cu_2O, CuCl
$FeCl_3$, $Fe(CO)_5$	$FeCl_2$, FeO
$PbCl_2$	Pb_3O_4, PbS
Hg, $HgCl_2$	
MoS_2	Mo_2O_3, MoO_3
$Ni(CO)_4$, $NiCl_2$	NiO
SeO_2, $SeCl_4$, Se, SnS_2	
$TeCl_2$	
	BaO, $BaCl_2$
	CdS, CdO
	CaO, CaC_2
	MgO, $MgCl_2$
	$MnCl_2$
	KCl, K_2SO_4
	NaCl
	TiO_2
	V_2O_5

Table 10. [illegible]

	A		B		C	D		E	
Element	[illegible]		[illegible]		[illegible]	[illegible]		[illegible]	
	Thompson	Logozzo	Thompson	Logozzo		Thompson	Logozzo	Thompson	Logozzo
Class I									
Be	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	475	0
Co	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0
Ge	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0
Mn	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	200	0
Ni	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0
Se	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0
Sn	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0
V	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	400	400
Class II									
Ag	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0
Cr	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	475	400
Cu	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	[illegible]
Fe	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	200	0
Mo	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0
Sb	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	0	0
Y	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	400	400
Zn	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	[illegible]	100	200

[illegible]

IV elements, no degree of control can be suggested a priori based on total particulate. Accordingly, we have indicated the degree of control that would be necessary to reach an acceptable environmental index as defined in the table.

Based on the "worst case" analysis, the elements listed below could be of concern. The key question is in what chemical form will these elements appear in either the combustion bed or in the flue gas. Where information of this type is available, it has been indicated.

- Arsenic (As)

  The volatility of As depends on the Ca content of the coal. With a large Ca content, As may be bound as the arsenate/arsenite and not volatized as As_2O_3.[1] This is the reason for the high retention of As when using a limestone/dolomite sorbent. On the basis of the emission factor for As in Table 10, however, As could still be emitted in harmful quantities. For example, in the case of bituminous coal, the uncontrolled emission factor is equivalent to approximately 10 ppm As (by weight).

- Beryllium (Be)

  Be is highly toxic (TLV = 0.002 mg/m^3). Its behavior in FBC is not yet understood. Argonne data suggest that beryllium is not enriched;[15] however, as shown in Table 10, there is some evidence that some Be could enter in the gas phase. $BeCl_2$ boils at 519°C;[16] hence, if Be is present as the chloride, it could vaporize. Therefore, mass balances of Be should be of high priority in FBC systems. Uncontrolled emission factors could be as high as 1 ppm Be by weight as indicated in Table 10.

- Lead (Pb)

  In conventional combustion lead is definitely enriched in fine particulates.[17] PbO_2 is not stable at combustion temperatures (decomposes at 288°C). PbO is stable to 882°C, but its vapor pressure is low (< 10 mm Hg).[18] $PbCO_3$ decomposes at 316°C.[20,21] Pb may exit as elemental lead, PbS, $PbCl_2$, or $PbSO_4$.

- Nickel (Ni)

  Ashing experiments suggest that nickel is not volatilized at FBC temperatures.[17] The presence of highly toxic nickel carbonyl is possible because of the high CO content in FBC flue gas. Its presence has been postulated in conventional combustion.[24] Because the suggested atmospheric limit for the control of exposure to nickel carbonyl is quite low, 0.3 ppb (2.1 ug/m^3),[25] nickel carbonyl should be studied experimentally.

  In fluidized bed gasification experiments, it has been found that 75 percent of the Ni in the fuel is tied up in the stone.[26] Similar data are not available for coal combustion.

- Uranium (U)

  Thermodynamic data show the oxide to be the stable form.[23] Uranium is not volatized in conventional combustion but there are no data on enrichment factors. Because of the concentrations of U in lignite coal, its pathways in FBC should be checked experimentally. As indicated in Table 10, uncontrolled emission rates could be as high as 11 and 56 ppm in bituminous and lignite coals respectively.

- Vanadium (V)

  The enrichment of V is small for conventional combustion, and hence should not be of concern in FBC. Thermodynamic data show that the oxide form is favored over the sulfate.[23]

  In gasification experiments, Westinghouse has found 100 percent retention of V on the spent limestone. This V concentration in the stone can range up to 1 weight percent.[26] This phenomenon should be studied for coal combustion.

- Halogens: Fluorine, Chlorine, Bromine

  Argonne has shown that F is captured by the limestone/dolomite bed by demonstrating that F retention was 5 to 23 percent with sorbent present. It is probably captured as CaF_2 (m.p. 1360°C).[20]

  Cl may be trapped as $CaCl_2$ (bp 1591°C). Chlorine will be emitted in the exhaust gas as HCl[15] and possibly in the form of NaCl. However, HCl emissions have not been noted at high concentrations. British studies show that Cl content of the exhaust gas is 20 ppm (W/W).[27]

Br may be captured in the bed as CaBr$_2$ (bp 806°C). Its lower boiling point could explain the higher emission factor noted by Argonne for Br than F.

Influence of Selected Process Options on the Fate of Trace Elements - This section discusses process variations and their possible effect on trace element emissions. Because this is not a well documented area, most of the discussion comprises recommendations for further research.

- Pressure and Temperature

  Pressurized FBC could modify trace element behavior. The vaporization of various elements or compounds could change significantly as pressure is increased. These changes could result from phenomena such as boiling point suppression, or shifts in chemical equilibrium concentrations. The difference in potassium loadings from the Argonne and British experiments may be a manifestation of the effect of pressure.

- Carbon Burn-Up Cell (CBC)

  Fly ash from the fluidized bed can contain as much as 20 percent unburned carbon. In some FBC designs, fly ash from the cyclones in the flue gas system will be returned to a carbon burn-up cell (CBC). The CBC can affect trace metal emissions because, it operates at a higher temperature than the fluidized bed (1093°C versus 816°C).

  At the higher temperature it is expected that some of the more active trace elements (Hg, Cl, Se, etc.) will be revolatilized or those in the unburned fly ash volatilized.

Gaseous Organic and Inorganic Compounds

Data on the specific organic or inorganic compounds formed during coal combustion are scarce. Analysis of combustion gases is usually limited to species such as CO, CO_2, SO_2, NO_x and, in some cases, total hydrocarbons. In addition to these combustion "end products," however, an extremely wide variety of other organic compounds could also form - especially during

transient operating conditions which often foster incomplete combustion. Predicting these products in the case of coal combustion is a difficult task. Detailed thermodynamic or kinetic calculations are of limited value because, for the most part, the actual reacting species are a matter of speculation and the extent to which true equilibrium is attained is often questionable. Some insight into potential organic pollutants, however, can be gained on the basis of a simple coal combustion model, the present understanding of chemical reactions in fluidized beds, and some simple thermodynamic calculations.

Simple Combustion Model - Conceptually, the combustion of a coal particle can be viewed in two steps as shown in Figure 4.

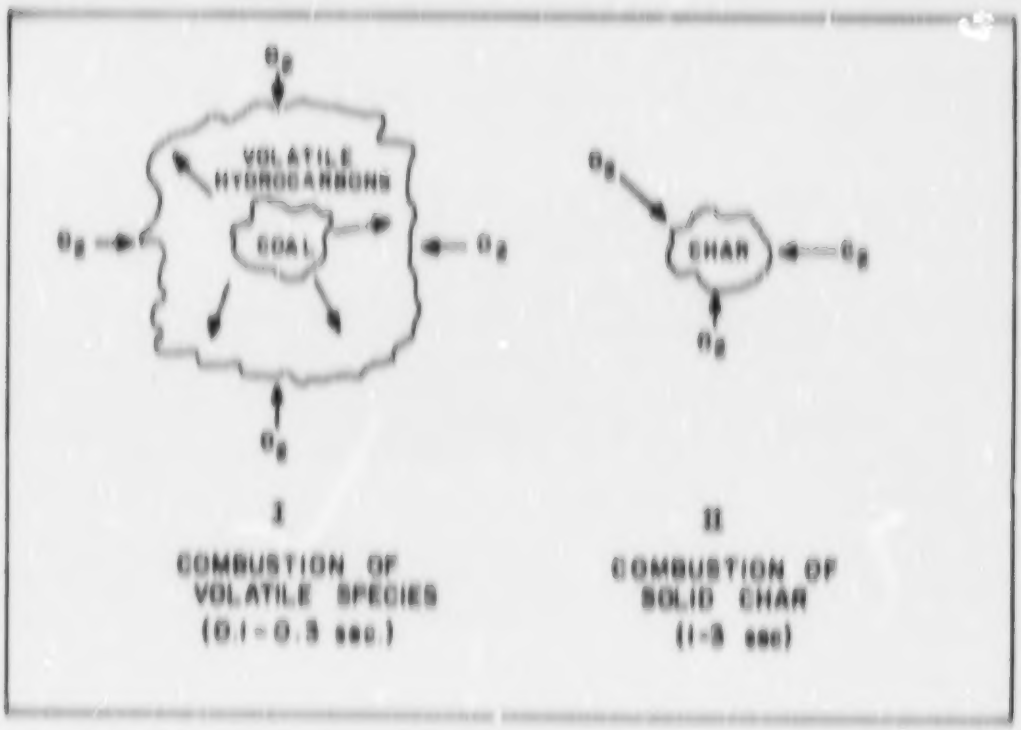


Figure 4. Schematic representation of coal combustion

In step I, volatile hydrocarbons are ejected from the coal particle; they mix with oxygen and burn in a cloud surrounding the particle. Both theoretical[31] and experimental[32] evidence indicate that this first step is completed in several tenths of a second or less. After devolatilization is complete, oxygen molecules attack the remaining char in step II, with burning here usually completed in times on the order of several seconds. The solid char in step II is predominantly carbon, although Sternling and Wendt[33] indicate that much of the chemically bound nitrogen in coal also winds up in the char. This char nitrogen probably burns to form NO, although the combustion mechanisms for heterogeneous combustion of nitrogen are not nearly as well studied as those for carbon. The main reaction product from heterogeneous carbon combustion is CO. The CO subsequently burns within the bed or in the freeboard to form CO_2. Some of these char particles are ejected from the bed but they are captured by the flue gas cyclones and returned for combustion in the carbon burn-up cell (CBC). Consequently, the crucial step for forming the more complicated organic species would be step I.

Volatile Products From Coal Decomposition - Potential organic pollutants can form because some of the products from step I could pass through the bed either completely or partially unburned. To estimate the extent to which this can occur, one must (1) determine the chemicals released from coal devolatilization, and (2) estimate the extent to which they will survive in a hot fluidized bed.

Figure 5 provides a convenient summary of the types of reactions that occur during coal decomposition. Coal has no unique structure; generally, it is viewed as a network of aromatic carbon compounds interspersed with various heterocyclic compounds containing oxygen, nitrogen, or sulfur. These heterocyclic compounds are less stable than aromatics and during pyrolysis these bonds tend to break first, as shown in Figure 5.

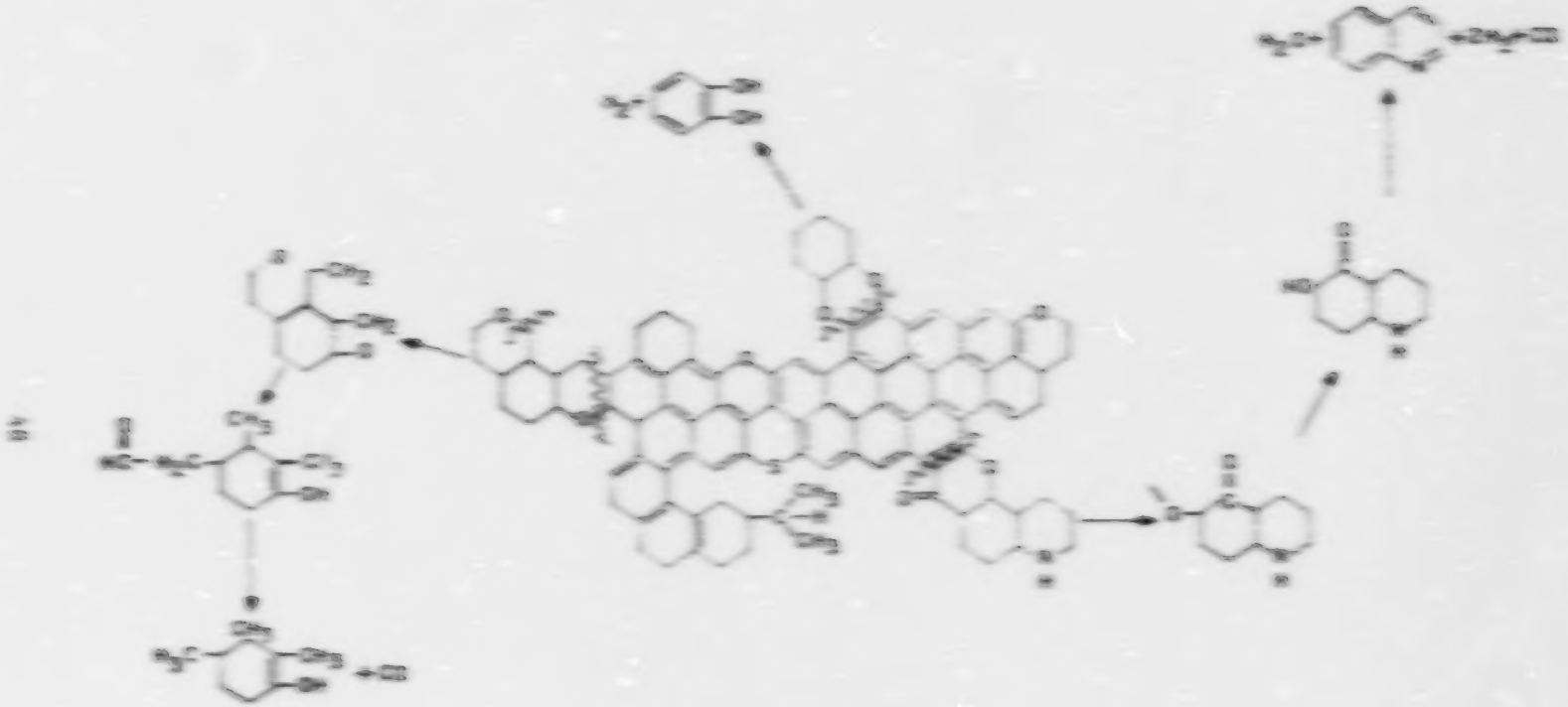


Figure 1. Schematic representation of coal pyrolysis[3a]

The product distribution in coal pyrolysis is temperature dependent. At temperatures on the order of 900°C (similar to those proposed for fluidized bed combustion) the predominant reactions are ring closures, condensation, and aromatization reactions. The main products tend to be polynuclear ring compounds with occasional nitrogen, oxygen, or sulfur substitution and simple compounds such as H_2, H_2S, NH_3, CH_4, etc.[34]

The overall synthesis of polycyclic organic compounds is shown schematically in Figure 6.[35] Coal combustion can be a source of these compounds[36,37] since, as seen previously in Figure 5, many of the products of coal decomposition are equivalent to the advanced stages of pyrene synthesis, shown below. (The extent to which these compounds might escape unaltered from the hot reaction zone of a fluidized bed will be discussed in the next section.)

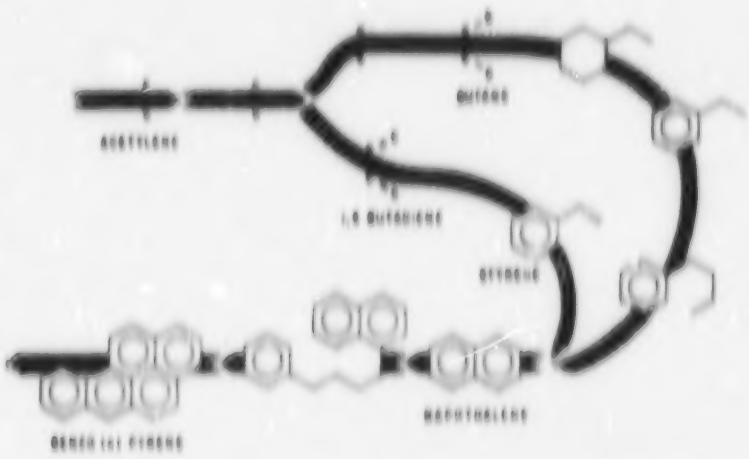
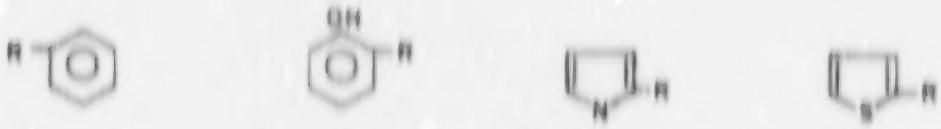


Figure 6. Pyrolytic synthesis of B(a)P[35]

During periods of start-up or shut-down, products from low temperature pyrolysis might also be encountered in a fluidized bed. These compounds tend to be single aromatic rings or heterocyclic compounds with alkyl side chains.[14] Examples shown below are substituted benzenes, phenols, pyridines, thiophenes, quinolines, where R = CH_3, C_2H_5, etc.



Using the above chemicals as starting materials, estimates can be made of which classes of compounds might survive in the reactive environment of a fluidized bed.

Combustion of Hydrocarbons - The predominant reaction of the volatile hydrocarbons, of course, will be combustion; the main question is to what extent combustion will be complete. As mentioned previously, both theoretical and experimental evidence indicate that combustion of volatiles will occur on the order of 100 ms. This is more than an order of magnitude less than the residence time in the bed; hence, there is certainly ample time for complete combustion. However, phenomena such as bubbling, slugging, uneven gas distribution, or localized reducing areas near the points of fuel injection could produce oxygen deficient zones from which unburned or partially burned hydrocarbons could escape. The extent to which this will occur will depend on the boiler design and could vary from reactor to reactor. Experimental tests indicate that the amount of unburned hydrocarbon in the flue gas has a strong dependence on the amount of O_2 present.[18] Some of the experiments are summarized in Figure 7. Note that at 1 percent O_2 in the flue gas (5 percent excess air), hydrocarbon concentrations are greater than 3000 ppm. With

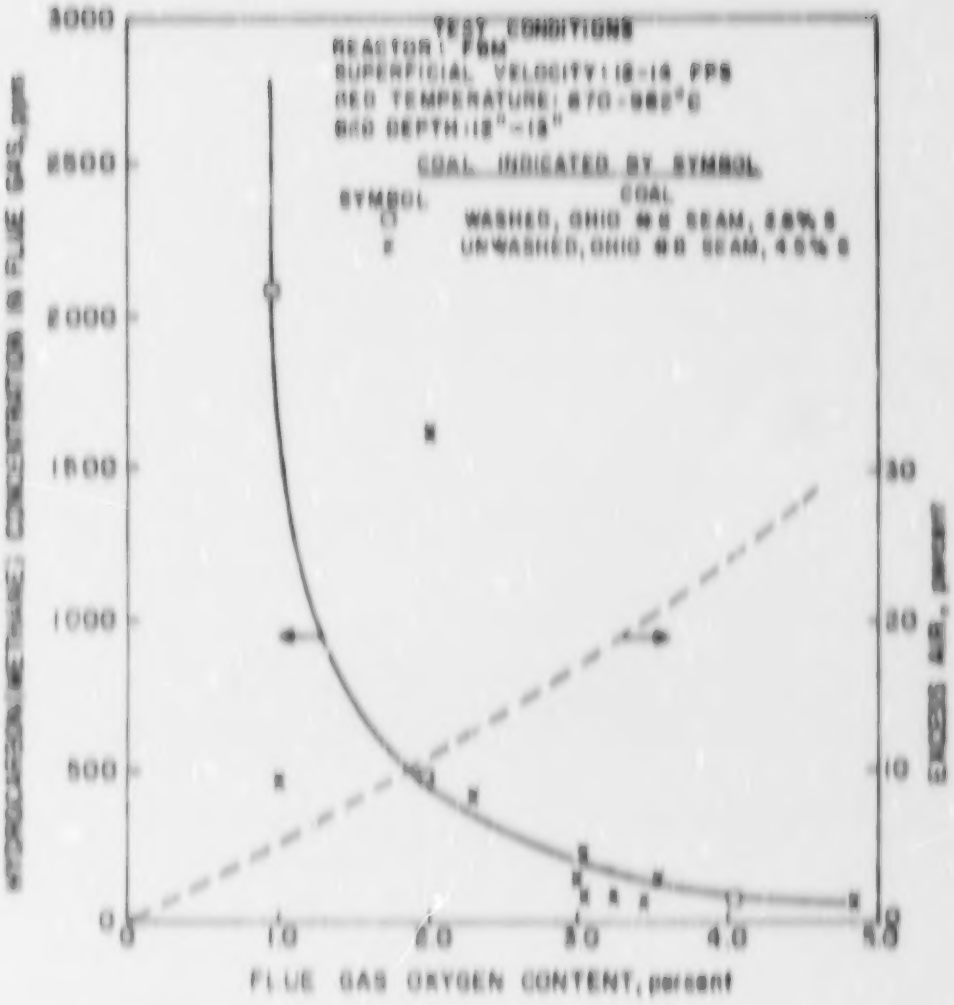


Fig. 7. Variation in hydrocarbon concentration with flue gas oxygen content in the fluidized bed module (FBM)[18]

O_2 flue gas concentrations on the order of 3 percent (17 percent excess air), hydrocarbon concentrations are reduced to 50 ppm. It is important to note, however, that these experiments were performed on a fluidized bed module (FBM) designed primarily for investigating heat transfer phenomena. The unit had a limited freeboard and was not necessarily designed for optimum combustion conditions. Hence, the results may be upper limits, but they do provide some insight into the generation of unburned hydrocarbons in FBC.

Products of incomplete combustion - Some insight as to the chemical composition of the products of incomplete combustion is provided below; the next section indicates methods which can be used to estimate concentrations of potential compounds.

- Hydrocarbons

  Fluidized bed reactors have long been used in the petroleum industry to "crack" or thermally decompose high molecular weight hydrocarbons. The process is shown schematically below:

  In these reactors, sand is often used as the bed material, sometimes with added catalysts such as oxides of V, Ni, and Cu. In some respects, a coal-fired fluidized bed combustor may be similar to a commercial cracker (including trace metals present as catalysts); hence one might expect that most unburned hydrocarbons would be extensively "cracked" by the time they leave the bed. Theoretical estimates of the first order rate constant for the cracking of a hydrocarbon of molecular weight 225 indicate that half the material will be cracked in 30 ms at 727°C.[3] In some respects, this could be a significant advantage of fluidized bed coal combustion versus conventional coal combustion. Coal-fired units (particularly small industrial or residential units) are significant sources of polycyclic organic compounds. In a fluidized bed, the increased gas-solids contact may enhance the tendency for these species "crack" to form compounds such as CH_4, C_2H_4, C_2H_6, etc. If, in fact, this is so, the probability of finding organic sulfur and nitrogen compounds such as thiophenes, mercaptans,

carbazoles, etc. should also be very small. These species will most likely decompose to form small hydrocarbons and species such as H_2S, HCN, and COS. Pyridine, for example, decomposes readily at temperatures on the order of 900°C to form HCN and hydrocarbons.[11]

- Oxygenated Hydrocarbons

Organic chemicals, such as ethylene oxide, phthalic anhydride, naphthaquinones and aromatic carboxylic acids, can also form via partial oxidation of hydrocarbons. An example is shown below:

naphthalene phthalic anhydride

These reactions, which are often used in organic syntheses, usually proceed only under very controlled process conditions and at temperatures on the order of 200 to 400°C; hence, their occurrence in a combustor operating around 900°C seems very unlikely. There could be some possibility of their occurrence during start-up and shut-down when temperatures are lower, but it seems unlikely. A tentative identification of diphenylene oxide in particulates from acetylene-oxygen and ethylene-oxygen flames, however, has been recently reported.[40]

- Carbon Monoxide (CO)

Carbon monoxide forms in the bed, but it usually burns there or in the freeboard to form CO_2. At 10 percent excess air, CO usually drops below 1000 ppm in atmospheric pressure fluidized bed units and below 200 ppm in pressurized units. High CO levels usually indicate significant gas-bypassing within the bed.

- Soot

Fuel-rich conditions lasting for only a short period of time can lead to the formation of a fairly significant quantity of soot which can take a long time to burn away again.[41] Soot particles tend to be exceedingly small and would not be collected by the cyclones of the electrostatic precipitator.

- Carbides

  It is also conceivable that metal carbides could form in a fluidized bed combustor. Calcium carbide (CaC_2), in particular, is formed by heating lime and carbon. Most carbides would not be volatile at the prevailing temperatures; hence, they should remain in the bed. If formed, they could present problems upon disposal of the stone since carbides release C_2H_2 upon hydrolysis.

- Halogenated Hydrocarbons

  There is considerable chlorine content in coal itself plus there are some indications that NaCl may be added to fluidized beds to enhance SO_2 scrubbing;[43] hence, the possible halogenation of hydrocarbons must be considered. At temperatures encountered in a fluidized bed combustor, however, chlorinated hydrocarbons most likely will not be stable. The effect of chlorination on the pyrolysis products of British coals has been investigated[43] and it has been found that at high temperatures, chlorinated tars are not produced. Practically all of the chlorine appears as HCl.

Concentration Estimates of Organic and Inorganic Compounds - Equilibrium calculations can be used to predict the composition of the combustion gases. The most commonly used method is the minimization of the chemical system's free energy.[44] This method can provide useful concentration estimates but is probably most useful for predicting trends or concentration ratios. In the case of fossil fuel, one usually uses the elemental composition as the starting material and the combustion products are usually limited to simple molecules (3 atoms or less). Calculations of this type have not been extensively applied to coal combustion, although they have been used in coal gasification analyses.[45] Because gasification is essentially incomplete combustion of coal, these analyses can be used to provide very conservative upper limits for the concentrations of "reduced" species such as COS, NH_3, and H_2S which may be present in combustion gases. Estimates based on gasification equilibrium calculations are shown in Table II.

Table 11. CALCULATED EQUILIBRIUM CONCENTRATION FOR SELECTED SPECIES PRODUCED BY INCOMPLETE COMBUSTION OF COAL[15]

Coal analysis: C = 68.5%, H = 5.5%, O = 8.5%, N = 1.4%, S = 4.1%

Oxygen present: 50% of stoichiometric requirements

Temperature: 760°C

Species	Mole fraction
H_2	0.16
CO	0.28
H_2	0.15
H_2O	0.05
CO_2	0.10
CH_4	0.06
H_2S	0.008
COS	0.0005
NH_3	0.0007
C(g), HCN, CS_2	$< 10^{-5}$
C_2H_2, C_2H_4, $(CN)_2$	
H_2, SO_2, SO_3	
NO, NO_2	

As the amount of oxygen in the combustor is increased, the concentration of "reduced" species decreases. The equilibrium calculations include a mass balance for each of the elements; hence, an extrapolation of the calculations to excess air levels on the order of 20 percent, where SO_2 is approximately 500 ppm, indicates that compounds such as H_2S, COS, and CS_2 should decrease by about two orders of magnitude. Similar consideration would apply to "reduced" nitrogen compounds; hence, a conservative upper limit for the concentration of compounds such as H_2S, COS, CS_2, SO_3, HCN, $(CN)_2$, and NH_3, under typical combustion conditions, is 1 ppm, which does not pose significant environmental problems.

Free energy minimization calculations for the more complicated hydrocarbons (e.g., polynuclear aromatics) are impractical because of the complexity of the chemicals involved. To estimate the concentrations at which these types of compounds might exist in the FBC flue gas, one can use empirical correlations between benzo(a)pyrene and CH_4 concentrations from measurements in conventional coal-fired combustion systems. Figure 7 indicates the variation of total hydrocarbons (as CH_4) as a function of O_2 concentration from one set of fluidized bed combustion experiments.[46] Under normal operating conditions, about 3 percent O_2 in the flue gas (20 percent excess air), the concentration of hydrocarbons (as CH_4) is about 100 ppm (volume/volume = V/V). Although emissions can often vary between different fluidized bed systems, 100 ppm provides a convenient reference value. Previous measurements with conventional coal-fired systems indicate that compounds such as benzo(a)pyrene are typically 10^{-5} times less than the concentration of total hydrocarbons as CH_4.[46,47] Using our reference value of 100 ppm (CH_4), this implies that in a fluidized bed system polynuclear aromatic hydrocarbons (PAH) could exist in the flue gas at concentrations (V/V) on the order of 1 part per billion (ppb). Considering that flue gases are typically diluted by about a factor of a thousand when they are emitted from the stack, this implies that ambient concentrations of PAH near FBC facilities would be on the order of 1 part per trillion. This corresponds to about 0.6 ng/m^3 which is roughly comparable to the natural background concentration ranges found in rural areas.[46,47] Accordingly, it seems that polynuclear aromatic hydrocarbon concentrations should not be high enough to cause problems.

Particulate Emissions

Only limited data on particulate emissions from fluidized bed combustion are currently available.[48,49] Preliminary data, using more sensitive particle sizing techniques than used previously, indicate that the mass median diameter of the flue gas particles (50 percent of the mass of the

particles are above that size) is about 7 μm in a pressurized system.[14] This means that significant concentrations of fine particles could exist in the flue gas. Further experiments on particle size distribution and chemical composition as a function of particle size should receive high priority. The following discussion summarizes currently available data on particulate loadings in FBC.

Atmospheric Pressure Fluidized Bed Combustion (APFBC) - For the process parameters shown below, Argonne Laboratories measured an average dust loading leaving the secondary cyclone of 0.06 grains/scf and a maximum loading of 0.22 grains/scf.

Flue gas flow rate:	8-14 cfm
Coal feed rate:	4-7.8 lb/hr
Additive feed rate:	1.1-2.3 lb/hr
Primary cyclone:	6-5/8 in. diameter
Secondary cyclone:	4-1/2 in. diameter
Dust loading (combustor exit):	0.16-1.78 grains/scf
Combined cyclone efficiency:	Approx. 90%.

Figure 8 shows the particle size distribution obtained from these experiments.

Experiments at the National Coal Board in England indicated dust loadings of 0.1 to 0.6 grains/scf when using primary and secondary cyclones having collection efficiencies of 90 percent at 10 μm.[19] These experiments also indicated that the particulate contained 5 to 15 percent carbon and 85 to 95 percent ash and additive.

Pope, Evans and Robbins made initial investigations of particle size distributions in FBC, as shown in Figure 9. In some of their experiments, NaCl (salt) was used as an additive to enhance SO_2 removal; the addition of NaCl also affected the particle size distribution as shown in Figure 9. No mechanism explaining the influence of NaCl on particle formation was postulated.

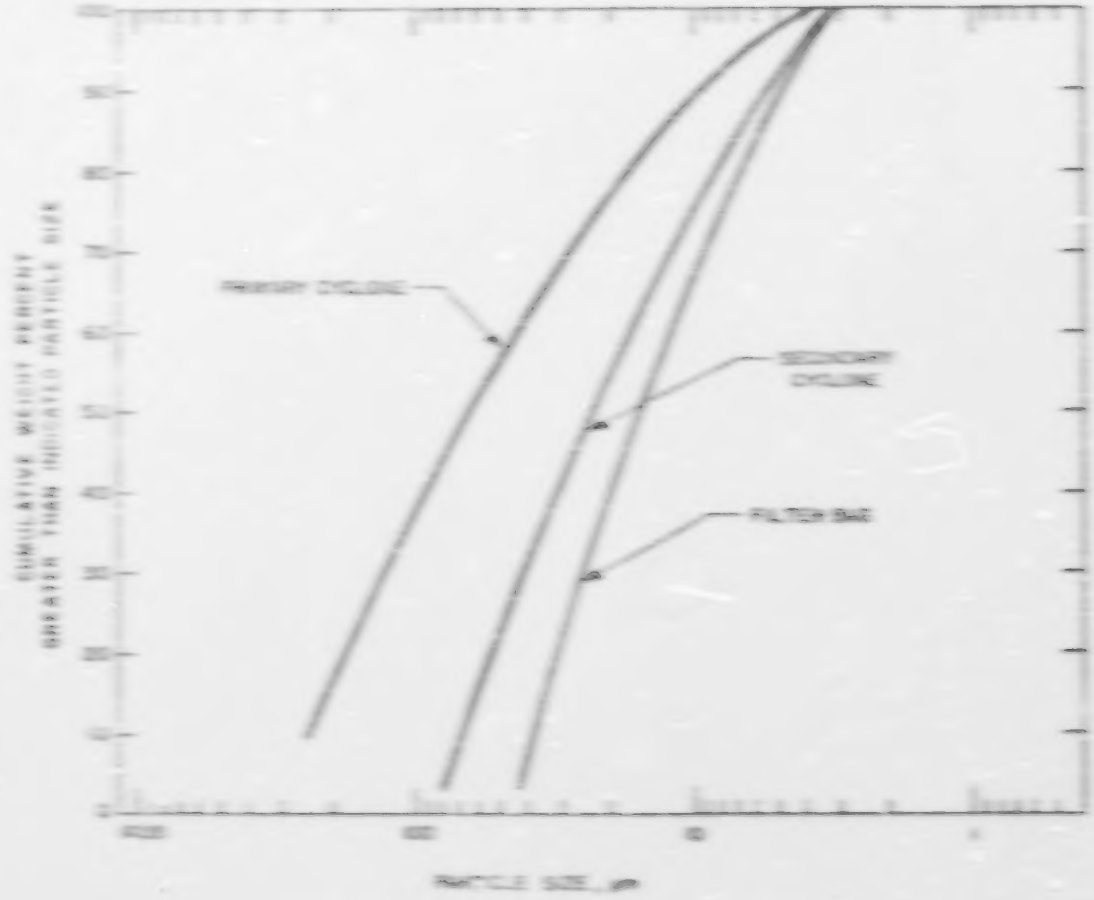


Figure 8. Typical particle size distribution of electrical material collected in primary cyclone, secondary cyclone, and fil-ter bag during period of additive injection[10]

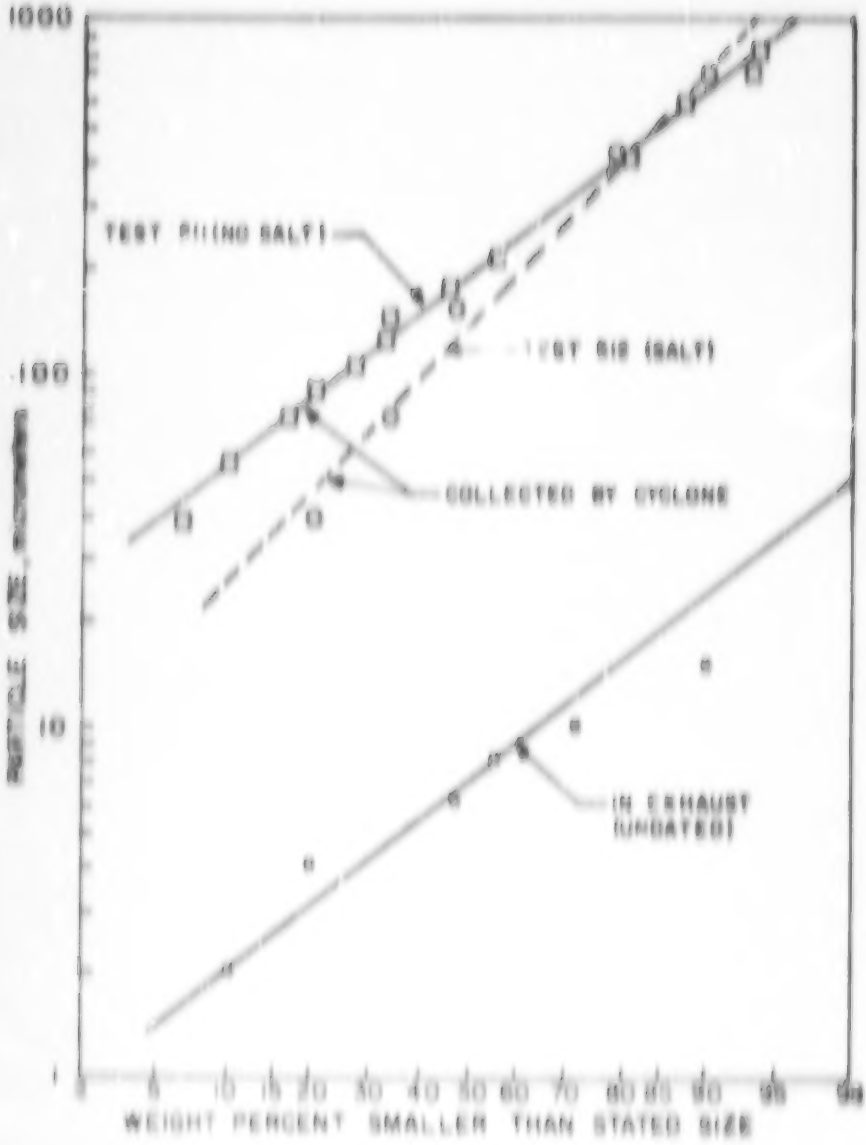


Figure 9. Fly ash size distribution for Pope, Evans and Robbins, Inc., atmospheric pressure fluidized bed combustion (AFBC)[15]

At the FBC demonstration plant currently under construction in Rivesville, West Virginia, Pope, Evans and Robbins will use a hot electrostatic precipitator to reduce particulate loading below the EPA limit of 0.04 grains per scf (0.1 lb/10^6 Btu). A hot (approximately 316°C) electrostatic precipitator is used because the high carbon content (as high as 20 percent) of the fly ash causes a high resistivity which makes operation of a cold precipitator inefficient.

Pressurized Fluidized Bed Combustion (PFBC) - A comprehensive study of the influence of selected process parameters on grain loadings in pressurized fluidized bed combustion was performed by workers at Argonne National Laboratories.[5] Their results for particulate loading as a function of fluidizing gas velocity and as a function of Ca/S mole ratio are shown in Figure 10.

The Argonne experiments indicated that, after passage through two cyclones, the solids loading in the flue gas ranged from 0.3 to 2.1 grains/scf. By adding a final filter, flue gas loadings were brought below 0.04 grains/scf - the EPA emission limit.

The above results suggest that particulate removal devices, in addition to the process cyclones normally used, will be required in order for fluidized bed combustion to meet EPA particulate emissions standards. As noted earlier, Pope, Evans and Robbins will use a hot electrostatic precipitator at their demonstration plant in Rivesville, West Virginia. Exxon is incorporating a granular bed filter in the pressurized mini-plant which shows promise of reducing fine particulate loadings substantially.

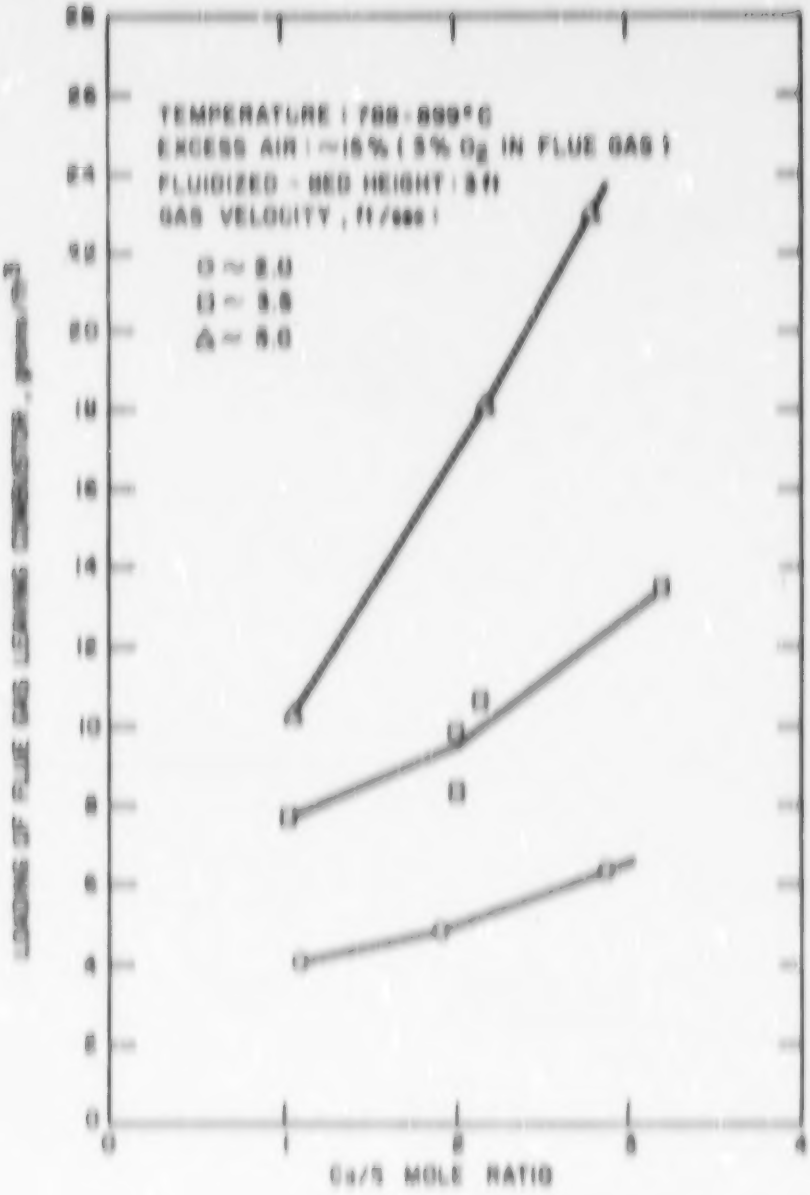


Figure 10. Solids loading of flue gas leaving the combustor in Argonne National Laboratory's pressurized fluidized bed combustion (PFBC)[1]

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SECTION V

POTENTIAL POLLUTANTS FROM AUXILIARY PROCESSES ASSOCIATED WITH FLUIDIZED BED BOILERS

LIMESTONE REGENERATION

The purpose of this discussion is: (1) to describe the methods of regenerating sulfated limestone produced in coal-fired fluidized bed combustion; and (2) to discuss the effects of regenerator operating variables on possible pollutant formation. At present, both one- and two-step processes are being considered; the one-step process can operate at either atmospheric or higher pressure, while the two-step system is associated with high pressure operations. Effluents from the regeneration process include flue gas, particulate matter in the flue gas, spent stone, and any emissions from the associated sulfur recovery plant. Leachates resulting from disposal of the spent stone could also be important.

One-Step Regeneration

Calcium sulfate is reduced by CO and H_2 via the following reaction:

$$CaSO_4 + \begin{bmatrix} H_2 \\ CO \end{bmatrix} \rightarrow CaO + SO_2 + \begin{bmatrix} H_2O \\ CO_2 \end{bmatrix}, \qquad (1)$$

The reaction proceeds rapidly at temperatures of about 1100°C and atmospheric pressure. (Regeneration is generally carried out at temperatures above 1100°C if operated under pressure (10 atm).)

The off gases from the regenerator can be sent to a Claus Plant to produce elemental sulfur, a sulfuric plant or a scrubber. The following reaction occurs in the Claus Plant:

$$2\ H_2S + SO_2 \rightarrow 2\ H_2O + 3S \qquad (2)$$

A portion of the sulfur can then be reacted with methane to produce H_2S which is reused in reaction (2). Figure 11 provides an example of the overall process flow for a one-step regeneration scheme based on a design by H. W. Kellog.[1] Westinghouse Research Laboratories have also designed a one-step regeneration scheme which is similar to that of Kellog, except coal is used as the source of reducing gas for the regenerator, instead of natural gas.[2] (Natural gas is a cleaner fuel than coal and would be expected to reduce the impact of any possible pollutants from regenerator; however, in the future it is expected to become increasingly scarce and possibly be unavailable for such applications.)

Two-Step Regeneration

The first step of this scheme involves the reduction of $CaSO_4$ to CaS with CO and H_2:

$$CaSO_4 + 4\begin{bmatrix} CO \\ H_2 \end{bmatrix} \rightarrow CaS + 4\begin{bmatrix} CO_2 \\ H_2O \end{bmatrix}, \qquad (3)$$

The reaction is generally carried out in the temperature range of 870 to 930°C and under high pressure. Calcium sulfide produced via reaction (3) is reacted with CO_2 and steam to produce $CaCO_3$:

$$CaS + CO_2 + H_2O \rightarrow CaCO_3 + H_2S, \qquad (4)$$

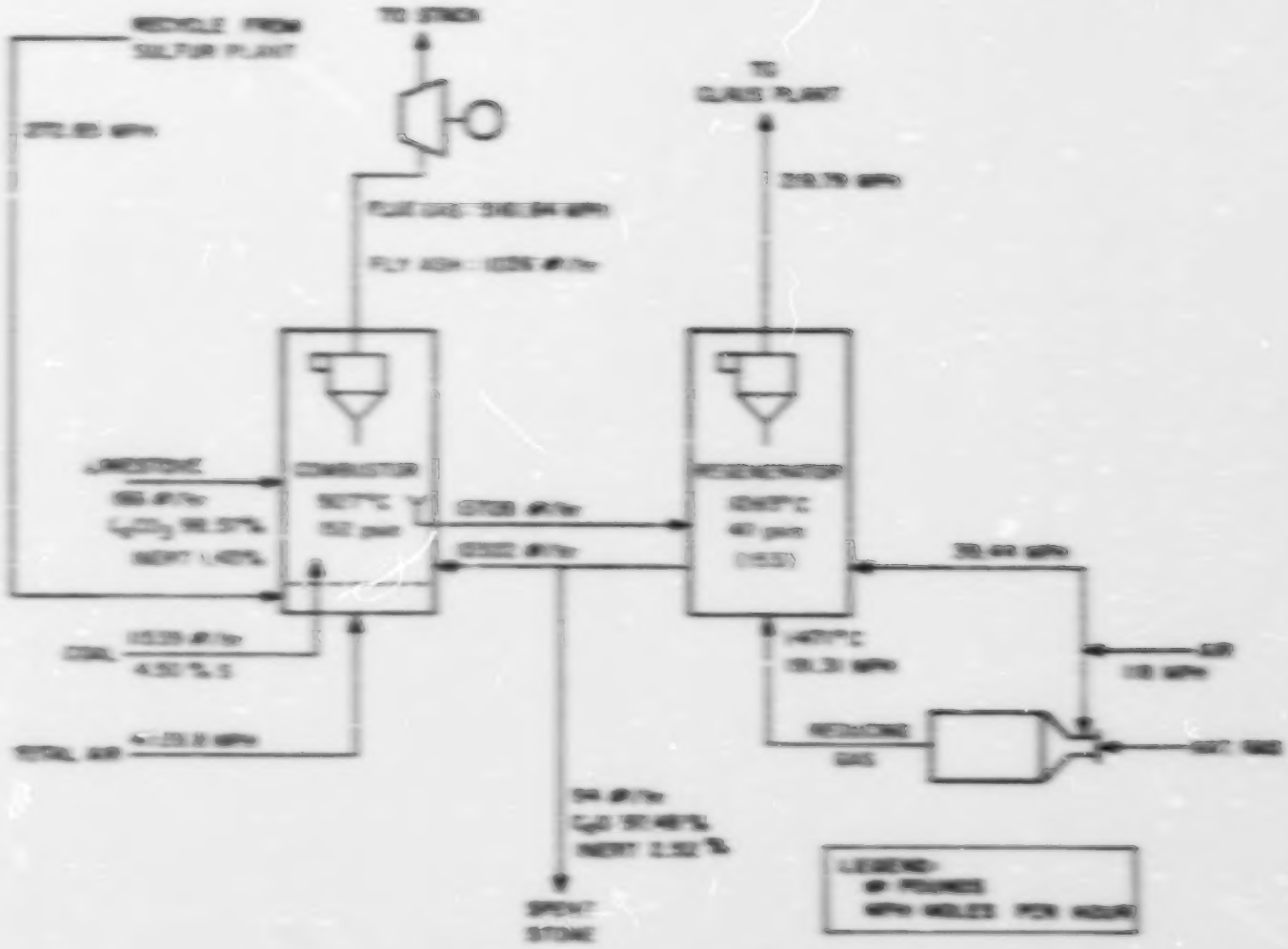

Figure II. 9. A. Exxon non-stop regeneration scheme[1]

Reaction (4) is usually carried out under pressure at temperatures of 540 to 710°C. Hydrogen sulfide can be further oxidized to produce SO_2 and/or elemental sulfur:

$$H_2S + 3/2\ O_2 \rightarrow SO_2 + H_2O \qquad (5)$$

or $$2H_2S + SO_2 \rightarrow 2H_2O + 3S \text{ (Claus reaction)}. \qquad (6)$$

Figure 12 shows a process flowsheet for a two-stage regenerator designed by M. W. Kellogg.[1] It illustrates the material flows involved; a similar design has also been proposed by Westinghouse Research Laboratories.[2]

Potential Pollutants From Limestone Regeneration

Because the regenerator is also a fluidized bed, it will behave in the same manner as the combustor with respect to operating variables. The main differences between the fluidized bed boiler and the regenerator is both the chemical nature of the reactants and the reaction conditions; i.e., chemical reduction as opposed to combustion. The feed to the regenerator will consist of CaO, $CaSO_4$, coal ash, and a reducing gas. Proposed sources of reducing gas have been natural gas or a mixture of CO, H_2 and CH_4 from gasified coal (i.e., incomplete combustion of coal). The use of natural gas should pose no significant environmental problems, but the future availability of natural gas for this type of operation is questionable, because of projected fuel shortages. The use of a "coal gas" for the regenerator could pose environmental problems. In using coal, especially under conditions of incomplete combustion, one has to be concerned about potential pollutants such as: trace elements, polycyclic aromatic hydrocarbons, fine particulates and inorganic compounds such as NH_3, H_2S, COS, HCN, CN, CS_2.

Some insight to fate of trace elements can be gained from equilibrium free energy calculations. Reactions of trace elements will be considerably

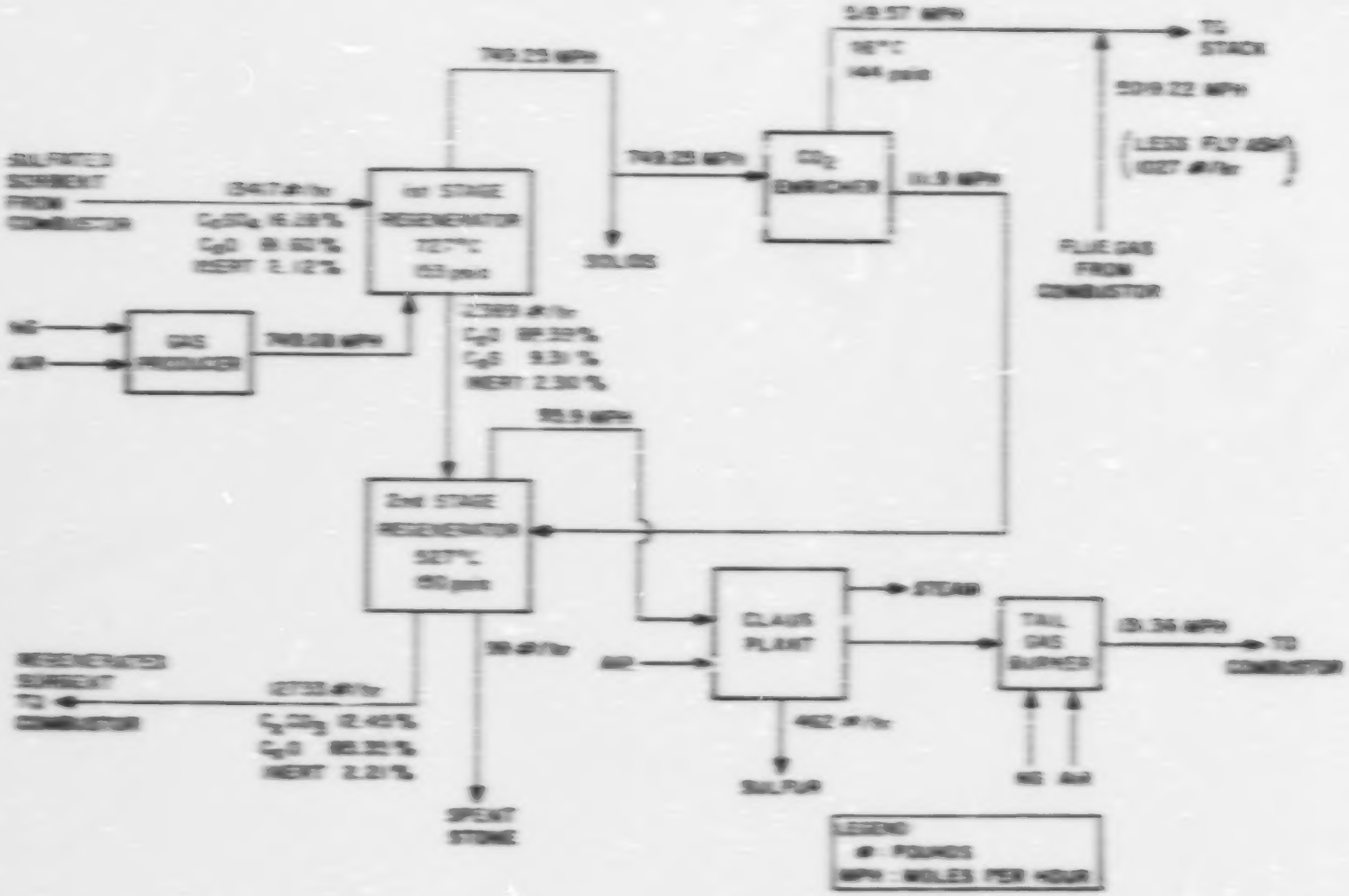

Figure 12. M. W. Kellog two-stage regeneration scheme[7]

different in the regenerator than those in the combustor. In the one-step regenerator the higher temperatures may cause vaporization of elements that did not vaporize in the combustor. Also, elements oxidized in the combustor and carried into the regenerator could undergo vaporization or further reaction.

Table 12 indicates possible chemical forms of trace elements based on free energy minimization calculations performed using reactive conditions similar to those in a limestone regenerator.[3]

Table 12. PROBABLE CHEMICAL FORM OF TRACE ELEMENTS IN THE REGENERATOR EXTRAPOLATED FROM FUEL GASIFICATION, FREE ENERGY MINIMIZATION CALCULATIONS[3]

Elements forming oxides or carbonates	Elements forming elemental vapors or volatile sulfides	
	Elemental vapors	Volatile sulfides
$MgCO_3$	Cd	Ba: Probably as BaS
MgO	Sn	Co: Forms CoS with excess CoO going to the metal
TiO_2	Pb	
$Zr(CO_3)_2$	Hg	Mn: Forms MnS and MnO
ZrO_2		Mo: Forms MoS with excess MoO forming Mo
Cr_2O_3		Be: BeO and BeS
Al_2O_3		Zn: Forms ZnO, ZnS, and elemental Zn vapor
CaO_2		
Li_2CO_3		
Na_2CO_3		
K_2CO_3		

In Table 17, those elements which form oxides or carbonates should not escape from the regenerator. Those forming elemental vapors, or volatile sulfides could escape. Referring to the "worst case" emissions of trace elements from combustion of coal discussed in Section IV, only Pb in Table 17 might pose a potential environmental problem. Equilibrium calculations to indicate the chemical form of other elements of concern from Section IV such as V, U, Be, Cl, and F, based on the "worst case" emission estimates were not available; hence, for discussion purposes, we simply assume those elements of concern with respect to direct combustion are also of concern in regeneration. (Note - the "worst case" estimates from direct coal combustion in Section IV do not strictly apply here because we do not have complete combustion of coal, but for the order of magnitude range of the estimates, they provide a useful reference.)

In addition to the information presented in Table 17, the following general observations can be made concerning the fate of certain trace elements.

- Arsenic

  Arsenic probably enters the REG in the form of calcium arsenate. In the REG it is reduced and volatized as arsenious oxide fume.[7] As_2O_3 vapor can enter the sulfur recovery unit and condense on small particulates. The As_2O_3 could also poison catalysts in the sulfur recovery plant or be leached from particulate collected by the cyclone.

- Vanadium

  Westinghouse has discovered, in their FB gasification studies, that V is completely trapped on the sorbent, probably as the oxide.[7] It is expected that the V will remain trapped on the sorbent in the REG.

There is no data available regarding the content of unburned organic compounds, polycyclic aromatic compounds and fine particulates which would be contained in the "coal gas" fed to the Regenerator. These species could conceivably escape from the regenerator in significant quantities. Most likely, they would pass into the sulfur recovery plant with the regenerator off-gases. Their fate there is also unknown. Experimental measurements of

the flow of these materials through the pilot regeneration process will be necessary before further evaluations can be made.

SOLID WASTE DISPOSAL

Solid waste disposal could prove to be one of the most significant obstacles to fluidized bed combustion simply because of the potentially large quantities of waste produced. Waste disposal requirements for several fluidized bed options have been investigated by workers at Battelle.[5] Their results are summarized in Table 13. The discussion here focuses mainly on the leachate potential of the solid waste.

Table 13. VOLUME OF SPENT BED PLUS ASH PRODUCED PER YEAR BY A 635-MW FBC PLANT[a,5] (acre-feet)

Ca/S mole ratio	Coal-sulfur content			
	1% sulfur in coal	2% sulfur in coal	3% sulfur in coal	4% sulfur in coal
Ca/S = 2	140	200	260	320
Ca/S = 1.2	119	150	195	235

[a]Assumptions: Coal feed rate = 430,000 pounds per hour;
Ash content = 12 percent;
90 percent SO_2 removal;
73 percent load factor;
Density of spent bed plus ash = 100 pounds per cubic foot (65 percent of theoretical density of spent bed mixture).

Experimental Studies

Leaching of the ash and stone from the combustor and regenerator poses a possible environmental hazard. Solid residue from the fluidized bed process consists of spent sorbent from the bed as well as a mixture of sorbent and fly ash removed from the flue gas by the particulate control equipment. If this material is placed in landfills, leaching by rainwater is possible. The British Coal Utilization Research Administration (BCURA)[6]

Pope, Evans and Robbins[7] and Westinghouse[8] have investigated the properties of the leachate obtained from the coal ash/limestone waste. BCURA found that, although CaO, MgO and CO_3 contents of the leachate varied, all their samples showed common features:

- High pH (10.5 to 11.6)
- High or complete extraction of sulfate
- Negligible extraction of magnesium.

The exposed surface tends to form an impervious crust as a consequence of carbonation/hydration. The preliminary BCURA tests indicated that disposal of lime-containing ashes is unlikely to pose serious problems. It is imperative, however, that tests using lysimeters and large field cells be performed.

In an attempt to find uses for fluidized bed by-products, Pope, Evans, and Robbins conducted leaching studies of the solids withdrawn from their fluidized bed.[8] The bulk of their withdrawn material, primarily lime anhydrite, with about 3 percent coal ash and the feed limestone have the composition shown in Table 14.

Pope, Evans and Robbins found pH values of 10.6 to 12.6 over a 4-day leaching study.[8] They also found that: less than 20 percent of the calcium was leached, less than 15 percent of the sulfate was leached, less than 10 percent of the sample was water soluble, and magnesium did not leach at all. Neither PEA nor BCURA reported trace element concentrations in their leachate samples.

Trace Metal Leaching

Theis, in a study on the potential trace metal contamination of water through fly ash disposal, has made the following assertions:[9]

- At the normal pH range of natural waters, the hydroxide of some metals (Hg, Pb, Cu, Cr, Cd, Zn) controls their solubility.

Table 14. COAL ASH[a] CONTAMINATION OF BENEFICIATED LIME/ANHYDRITE

Element	Raw limestone no. 1359	Lime/anhydrite
Ca	38.8 percent	39.0 percent
Mg	0.51 percent	0.43 percent
Fe	0.101 percent	0.42 percent
Al	0.15 percent	0.42 percent
Si	0.23 percent	1.14 percent
Na	0.027 percent	0.20 percent
K	0.08 percent	0.34 percent
Ti	0.012 percent	0.0380 percent
Zn	4.0 ppm	35.0 ppm
Cu	10.0 ppm	35.0 ppm
Ni	36.0 ppm	195.0 ppm
Cd	28.0 ppm	90.0 ppm
Pb	43.0 ppm	180.0 ppm
As	70.0 ppm	-
P	1.6 ppm	1.6 ppm

[a]Scrubbley coal ash = 9.5 percent aluminum. On this basis, the lime/anhydrite contains approximately 3 percent coal ash.

- At elevated pH, carbonate may control solubility.
- In general, trace metals display drastically decreased solubilities with increasing pH.
- In the pH range of 7 to 8.5, only Zn and Cd could be considered soluble.
- Arsenic is generally very soluble.

Theis presented the relationship between solubility and pH as shown in Figure 13.

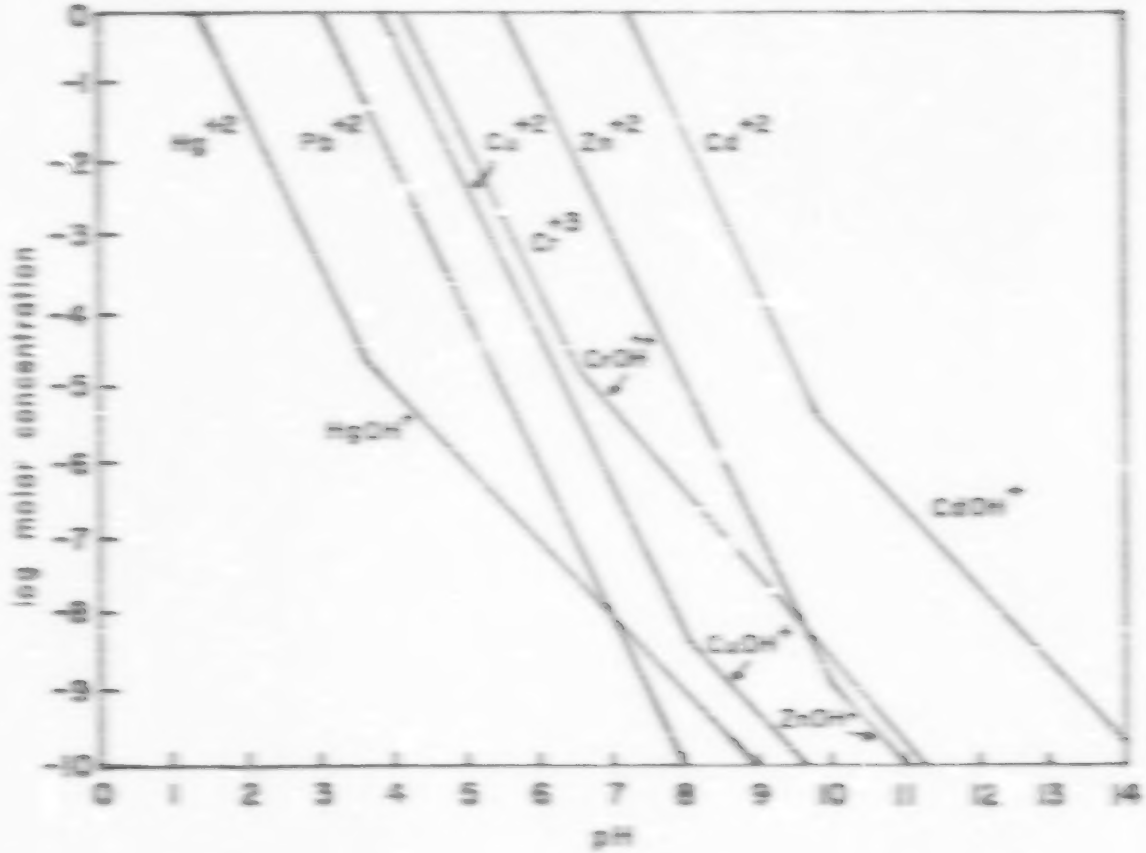

Figure 13. Solubilities of trace metals - free aquoic and mono-hydroxo complexes only considered[4]

The elements of major concern seem to be As, V, and Cd. However, since complexes may form which would increase the solubility of the metals, Pb and Hg, at least, may also be of concern in leachates. Theis found, for example, that addition of EDTA to his ash samples increased the solubility of all elements but mercury.[9]

Rossoff and Rossi have investigated the fate of trace elements in scrubber sludges.[10] Although the composition of a scrubber sludge is different than that of the spent stone from a regenerator or from the combustor, in general, the same elements are present and should be affected by pH and complexing agents in a similar manner. Table 15 lists metal solubility as a function of species present in weakly alkaline solutions.

The studies done by BCURA and PEU with partially sulfated lime (bed material) and coal ash have shown that the leachate is highly alkaline (high pH). Since metal solubility decreases with increasing pH, leaching from the fluidized bed combustion ash may be suppressed. Increased solubility may, however, occur by means of complex formation. No data were available on complex formation in the leachate from either spent stone or bed material.

In general, data are lacking on the leaching properties of trace constituents of the residue. Substantial lysimeter and field cell testing has not yet been conducted on residue from once-through and regenerative fluidized bed combustion systems. Therefore, much more data are needed before conclusions can be drawn regarding the environmental impact of FBC residue disposal.

EPA is continuing their program to assess the environmental impact of FBC solid residue disposal. Projects in this program are being conducted by Westinghouse, Ralph Stone and Co., and TVA.

Table 15. RELATIVE SOLUBILITIES IN NEARLY ALKALINE SOLUTIONS[a]

Cations	Trace anions		Major anions			
	AsO_3^-	SeO_3^-	Cl^-	OH^-	NO_3^-	SO_4^-
Major:						
Ca^{2+}	Slightly soluble	Insoluble				
Mg^{2+}	a	Insoluble				
Trace:						
Be^{2+}			Soluble	Insoluble		Insoluble
Cd^{2+}			Insoluble	Insoluble	Slightly soluble	Soluble
Cr^{3+}			a	Insoluble	a	Insoluble
Cu^{+}			Insoluble	Insoluble	Slightly soluble	Soluble
Hg^{+}			Insoluble	Insoluble	Insoluble	Slightly soluble
Pb^{2+}			Insoluble	Slightly soluble	Insoluble	Insoluble
Zn^{2+}			Very slightly soluble	Insoluble	Slightly soluble	Soluble

[a] Data to be determined.

FUEL STORAGE AND HANDLING

Electric utility plants and other intensive consumers of coal store large quantities in outdoor piles. Storage practices for fluidized bed combustion systems will be similar. Air emissions of particulates occur from wind erosion and handling operations. Air emissions of carbon monoxide and hydrocarbons will result during spontaneous combustion of reactive coals. Rain water draining through storage piles will also leach certain elements, creating potential ground and surface water pollution problems.

Coal Storage Requirements

Coal-fired electric utility plants maintain a 75- to 90-day coal supply on-site.[11,12] Typically, a 90-day coal supply amounts to 816 tons per megawatt (MW)[a] of generating capacity for a plant with an average load factor of 90 percent. Normal height of a storage pile is 30 feet, and the land area required is 0.04 acres/MW.[13]

Coal Pile Drainage and Leachates

Rain and snow cause water to drain through coal piles. Therefore, the magnitude of this problem will vary widely depending on plant location. The national coal pile drainage volume is reported to be 7.9×10^9 gallons (30×10^6 m^3) per year based on average rainfall[14] indicating a typical value of 40,000 gallons per year per MW. Available data on pollutant concentrations are presented in Table 16. The wide ranges are attributable to variations in coal properties as well as rainfall and drainage

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[a]MW as used in this report represents the electrical output of the system. The term "heat rate" - British Thermal Units of fuel per kilowatt hour of electricity (Btu/kWh) - is commonly used in the utility industry to denote plant performance. The 1975 average heat rate was 10,400 Btu/kWh, and the average coal heat content was 24×10^6 Btu/ton. New conventional coal-fired power plants, combined cycle plants and fluidized bed combustion systems may achieve heat rates below 9,500 Btu/kWh range.

rates. Although the drainage volumes discussed above were yearly rates, this does not imply constant flows. Actually, the drainage flow rate may vary greatly from day to day depending on rainfall. The highest pollutant concentrations and lowest pH will be associated with low drainage rates.

Table 16. COMPOSITION OF DRAINAGE FROM COAL PILES[15]

	Concentration, mg/l[a]
Alkalinity	15 - 86
BOD	1 - 10
COD	100 - 1,000
Total solids	1,500 - 45,000
Total suspended solids	20 - 1,300
Total dissolved solids	700 - 44,000
Ammonia	0.4 - 1.8
Nitrate	0.3 - 2.3
Phosphorus	0.2 - 1.3
Turbidity	6 - 505
Acidity	10 - 27,800
Total hardness	135 - 20,000
Sulfate	20 - 480
Chloride	825 - 1,200
Aluminum	0 - 16
Chromium	1.6 - 3.9
Copper	0.4 - 2.0
Iron	90 - 180
Magnesium	160 - 1,360
Sodium	2.2 - 8.0

[a]Appropriate for all values except pH. Using the volumes and conditions discussed in the text, 1 mg/l is equivalent to 0.33 lb/yr/MW.

Coal pile drainage can be controlled. Ground water contamination can be minimized by storing the coal on an impervious base of clay or plastic liner. Surface water runoff from coal piles can be collected by a drainage system and treated before discharge. Treatment often includes neutralization with lime, soda ash or alkaline waste streams from other processes. Clarification involves extended retention time and addition of coagulants if necessary.

Air Emissions From Coal Storage and Handling

Air emissions from coal storage include fugitive dust, carbon monoxide and hydrocarbons. Carbon monoxide and hydrocarbon emissions are a result of spontaneous combustion and have not been quantified. Particulate emissions consist of coal dust and are affected by wind speed, precipitation-evaporation, coal characteristics and coal pile geometry. Available data indicate an emission factor of 0.80 lb/ton/year.[17] Transport and handling operations represent two-thirds of the emissions from aggregate storage piles.[16] Therefore, total particulate emissions from coal storage and handling may reach 0.0016 lb/ton/year. Based on the previously discussed storage requirement, particulate emissions will be 3 tons/year/MW.

COAL DRYING

Hot air is used to remove the surface moisture from coal prior to crushing or pulverizing.[17] The inherent moisture in the coal is not usually affected by drying. Usually the coal is cleaned and dried at the mine, not at the consuming facility. Drying air temperatures of 316°C may be used. Particulate emissions from coal drying, before the application of control equipment, are in the range of 16 to 25 lb/ton, depending on the type of dryer used.[18] Control equipment efficiency commonly ranges from 70 to 99 percent.

COOLING SYSTEMS

The cooling requirements for electric power plants vary widely depending on the type of plant and the design efficiency. Lower efficiencies usually mean more heat losses to cooling water. The primary factor affecting the efficiency of a steam electric plant is the steam turbine efficiency which increases as the steam pressure and temperature increase. Gas turbine plants do not require cooling water as all the waste heat is rejected through the flue gas directly to the atmosphere.

The average steam electric plant operates at a fuel-to-electricity efficiency of 33 percent, requiring 10,400 Btu of fuel per kilowatt-hour (kWh) of electricity produced. Waste heat amounts to 67 percent (7,100 Btu/kWh) of the input, with 15 percent (1,600 Btu/kWh) attributable to inplant and flue gas losses and 52 percent (5,500 Btu/kWh) lost to the condenser cooling.[19] The steam turbine in the above case operates at about 40 percent efficiency based on a total heat input of 8,900 Btu/kWh and conversion of 3,400 Btu/kWh to electricity and 5,500 Btu/kWh rejected to the condenser.[19,20]

The cooling requirement for plants using gas turbines and steam turbines in the same cycle (combined cycle plants and pressurized fluidized bed systems) will depend on the heat input to each turbine. Cooling water losses equivalent to 60 percent of the energy input to the steam turbine will be required for high pressure steam turbines.

Cooling can be provided by once-through or recirculative systems. Most large new steam electric plants will be required to use recirculative systems.[21] An average plant using once-through cooling with a normal temperature rise of 8°C requires a water flow of 10^6 gal/day/MW and discharges 1.3 x 10^8 Btu/day/MW of added heat to the receiving waters.

Recirculative systems are used to minimize the heat discharged to surface waters. The following discussion is directed primarily to wet cooling

towers, although dry cooling towers, spray ponds and canals are also used or under development. A cooling tower recirculates a large volume of water (about 10^6 gal/day/MW) through the condenser and discharges the heat acquired to the ambient air by evaporation (75 percent) and direct heat transfer (25 percent). Therefore, for the present example, 10^8 Btu/day/MW must be discharged through evaporation equivalent to 13,000 gal/day/MW of evaporation.

Cooling tower make-up water for the water lost through evaporation, drift, and blowdown must be provided. Drift ranges from 0.005 to 0.02 percent of the flow for a well-designed tower.[31,32] The amount of blowdown (B) depends on the allowable cycles of concentration (C = the number of times the concentration of any constituent is multiplied from its original value in the make-up water), the evaporation (Ev), and the drift (D) as follows:

$$C = (B + Ev + D)/B \text{ or } B = \frac{Ev + D}{C - 1} .$$

For typical make-up water quality, C averages from 4 to 6, although the total range is 1.2 to 15. Continuing the above example for C = 5, Ev = 13,000 gal/day/MW, and D = 0.000125×10^6 gal/day/MW, then B = 29,000 gal/day/MW. Total make-up water required is then 15,000 gal/day/MW compared to 10^6 gal/day/MW for once-through cooling. Heat discharge can be eliminated by cold side blowdown and is greatly reduced compared to once-through cooling even when hot side blowdown is practiced.

Many chemicals have been used and are continuing to be used in recirculative cooling systems. Table 17 is a list of some common chemicals used in recirculative cooling systems.[33] Table 18 presents concentrations of corrosion inhibitors that are found in recirculative cooling systems.[34] Blowdown treatment is used to limit pollutant discharges. Additional potential pollutants include fogging and noise, as well as make-up water treatment wastes. Further information is available through many sources including references 26 through 36.

Table 17. CHEMICALS USED IN RECIRCULATIVE COOLING WATER SYSTEMS[24]

Use	Chemical
Corrosion inhibition or scale prevention in cooling towers	Organic phosphates Sodium phosphate Chromates Zinc salts Synthetic organics
Biocides in cooling towers	Chlorine Hydrochlorous acid Sodium hypochlorite Calcium hypochlorite Organic chromates Organic zinc compounds Chlorophenates Thiocyanates Organic sulfurs
pH control in cooling towers	Sulfuric acid Hydrochloric acid
Dispersing agents in cooling towers	Lignins Tannins Polyacrylonitrile Polyacrylamide Polyacrylic acids Polyacrylic acid salts
Biocides in condenser cooling water systems	Chlorine Hypochlorites Sodium pentachlorophenate

Table 18. COOLING TOWER CORROSION AND SCALE INHIBITOR SYSTEMS[15]

Inhibitor system	Concentration of chemical additives in recirculating water, mg/l
1. Chromate	200 - 530 mg/l CrO_4
2. Chromate + Zinc	17 - 65 mg/l CrO_4 8 - 35 mg/l Zn^{++}
3. Chromate + Zinc + Phosphate (inorganic)	10 - 15 mg/l CrO_4 8 - 35 mg/l Zn^{++} 30 - 45 mg/l PO_4
4. Zinc + Phosphate (inorganic)	8 - 35 mg/l Zn^{++} 15 - 60 mg/l PO_4
5. Phosphate (inorganic)	15 - 60 mg/l PO_4
6. Phosphate (organic)	15 - 60 mg/l PO_4 1 - 10 mg/l organics
7. Organic Biocide	30 mg/l chlorophenol 5 mg/l sulfone 1 mg/l thiocyanate

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SECTION VI

SUGGESTED CONTROL TECHNOLOGY FOR FBC SYSTEMS

INTRODUCTION

Flue gas emissions and solid waste disposal are the two major aspects of fluidized bed combustion (FBC) of coal which may require special control technology. If sulfur recovery techniques are employed in processing spent stone, tail gases from the recovery unit may also require pollution control devices.

Flue gas emissions will include both gases and particulates, and the relative concentrations may vary from unit to unit. In addition, different control options may be available depending upon whether or not one is dealing with an atmospheric or a pressurized combustion system.

Control technologies for flue gases and solid waste are discussed below.

FLUE GAS TREATMENT: AND-ON CONTROL TECHNOLOGY

The discussion here is broken down into gaseous emissions and particulates. Primary emphasis is given to particulate control, because this seems, at this time, to be the major area in which problems may arise. Some gaseous emissions could be troublesome but control techniques for those gaseous pollutants that have been defined seem straightforward; hence, they are discussed only briefly here. The discussion on particulate control is subdivided into options for atmospheric or pressurized operation. Because FBC systems are being designed to operate in the post-1980 era

when emissions standards may be stricter, control equipment capable of collecting fine particles (< 3 microns diameter) at high efficiency has been emphasized.

Particulate Control Equipment for Atmospheric Pressure Combustion

The major source of particulate emissions from a FBC system will be the combustor (including the optional carbon burn-up cell). Schematic diagrams of the important system components for particulate control are shown in Figures 14 and 15. Much of the elutriated bed material will be in the form of large particles, 100 to 1000 μm, and will be collected by the cyclones. Particulate loadings after the cyclones, however, will still be high enough to warrant additional control. As discussed earlier, one problem in the current analysis is that data on particulate emissions from FBC, particularly fine particulates (< 3 μm) are very limited at this time, so that the actual degree of control needed even to meet current standards is not known precisely.

General Comments on Control Devices - The performance of a cyclone depends on a variety of factors including the particle shape and size, the cyclone dimensions, gas velocity and gas viscosity.[1] Multiple small diameter cyclones are most effective, but, as illustrated by the data in Table 19, cyclone efficiency decreases rapidly as particle size decreases.[2]

Cyclone efficiencies decrease rapidly for particle sizes below 5 microns, dropping to about 20 percent for a 2-micron particle and a 6-inch diameter cyclone. For effective control of fine particles, more sophisticated equipment must be used.

Three control devices are now commercially available for controlling fine particulates (< 3 microns): electrostatic precipitators, scrubbers, and fabric filters. Choosing an appropriate control device requires consideration of a number of variables; e.g., aerosol properties, available space, efficiency objectives, water pollution regulations, energy costs, etc.

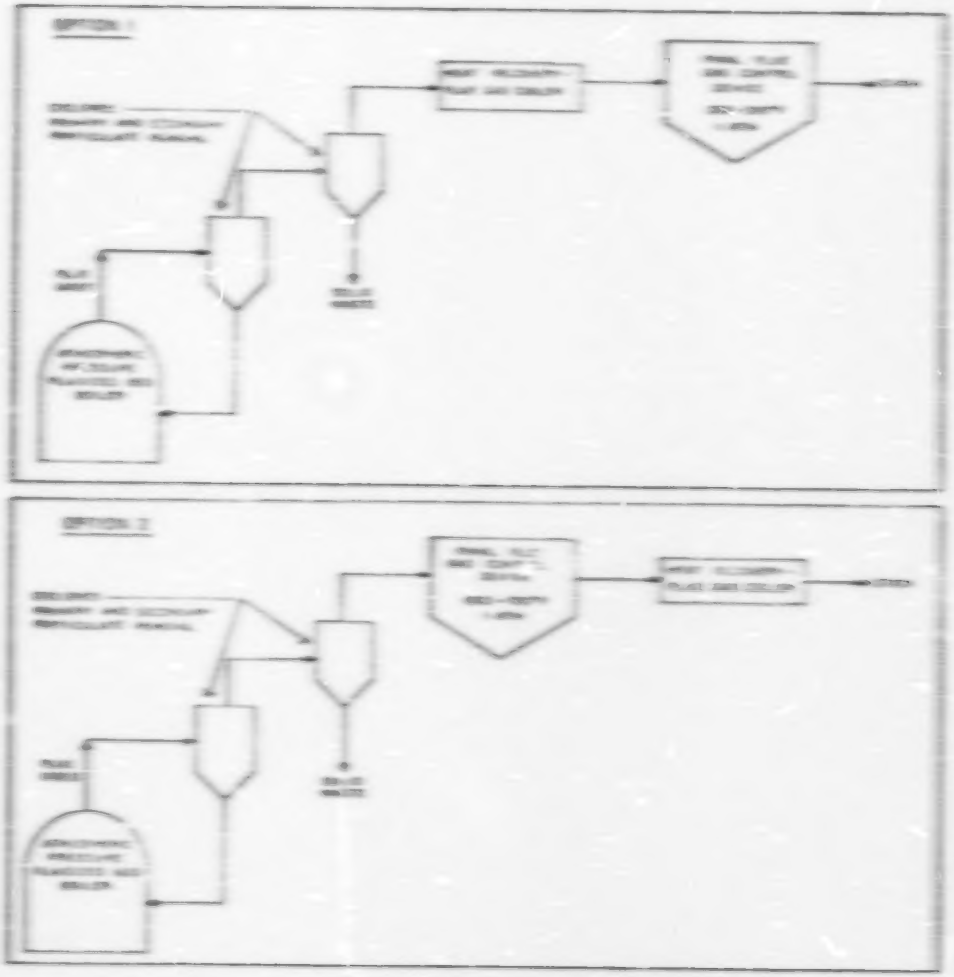

Figure 14. Control of flue gas emissions from an atmospheric pressure FBC boiler

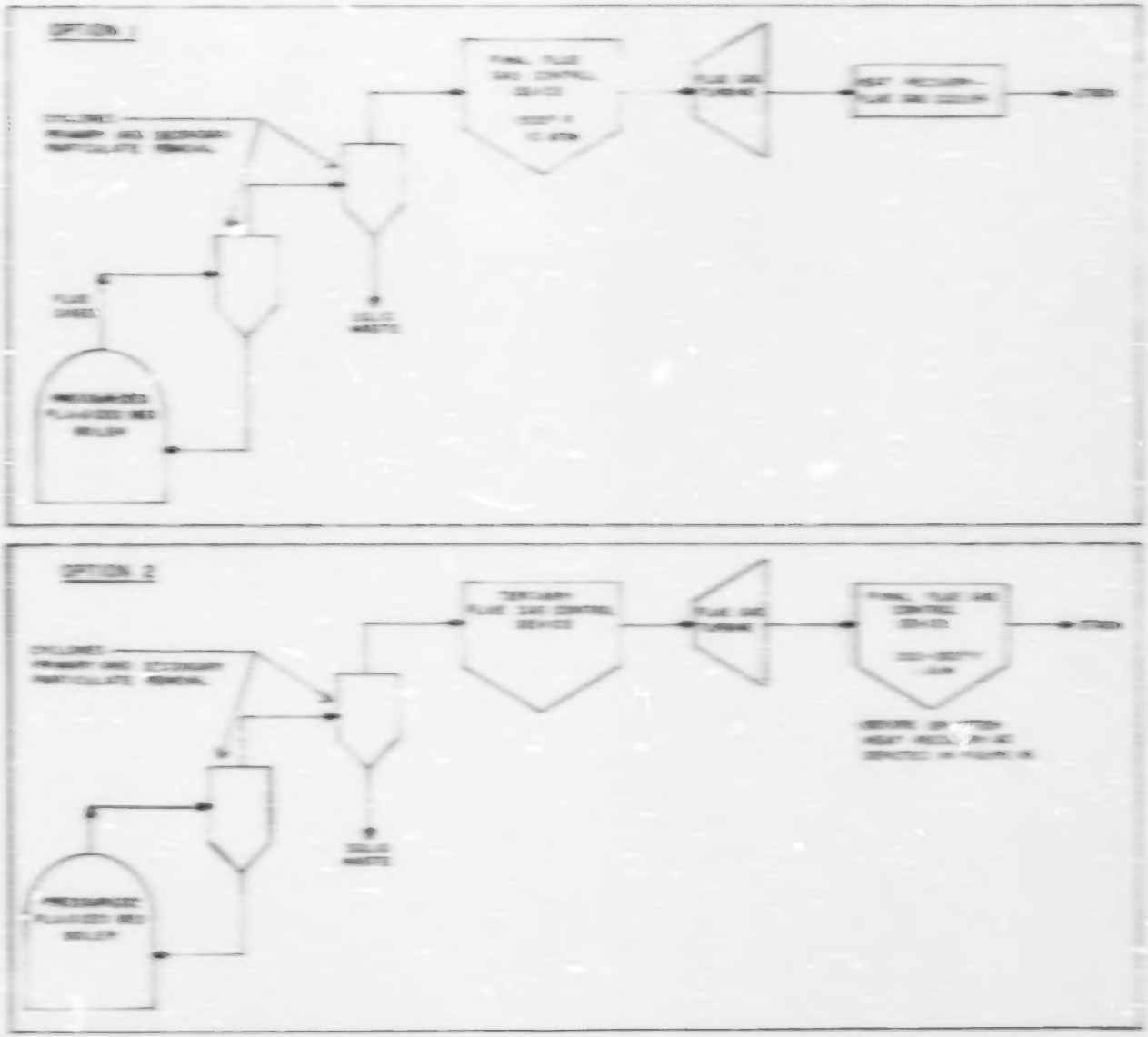

Figure 15. Control of flue gas emissions from a pressurized FB boiler

Table 19. DISTRIBUTION BY PARTICLE SIZE OF AVERAGE COLLECTION EFFICIENCIES FOR VARIOUS PARTICULATE CONTROL EQUIPMENT

Type of collector	Collection efficiency, %, Particle size range, μm				
	<5	5 to 10	10 to 20	20 to 44	>44
Simple cyclone	7.5	28	43	80	90
Multiple cyclone (12-in. diameter)	35	54	74	95	98
Multiple cyclone (6-in. diameter)	83	95	98	99.5	100

For electric utility coal-fired boilers, electrostatic precipitators (ESP) are the most common final control device.[3] ESP's have proved to be reliable, have a low operating cost, and perform at reasonably high efficiencies. Venturi scrubbers are used much less frequently because the efficiency tends to be low for fine particles, unless high pressure drops and thus large amounts of energy are used. Fabric filters have been used in only two utility coal boilers over the past 2 to 3 years,[4,5] with a third larger unit scheduled to be installed on a 330-MW boiler.[6] Fabric filters are attractive because of very high efficiencies (99.8 to 99.9 percent)[4,5] at competitive costs.[7] In the past, however, fabric filters were not used on coal-fired boilers because of questionable reliability as a result of fabric deterioration. In addition, particulate control devices with maximum efficiencies of 99.9 percent were not needed and are still not required in many cases. New power plants are now being designed to achieve particulate control efficiencies in the 99 to 99.5 percent range; hence, a reasonable goal for FBC systems would be control efficiencies of at least 99 percent and probably 99.5 percent.

In FBC, the most important coal ash properties affecting fine particulate control are the particle size distribution, the mass concentration, the SO_3 concentration, and the particle resistivity (for ESP). Generally

the smaller the particle, the more difficult it is to collect. The dependence of collection efficiency on particle size is most pronounced for scrubbers; it tends to be less restrictive for fabric filters and electrostatic precipitators. Figure 16 presents the predicted particle size distribution at the inlet to the final control device[8,9] of an overall fluidized bed combustion system (shown previously in Figure 14).

Large variations in size distribution may result from coal ash properties and the design of the cyclone precollectors. A composite of the particle size distribution from many conventional pulverized coal systems having only cyclone or similar mechanical control systems is also presented in Figure 16. Because the particle size data are extremely limited for fluidized bed systems, one can conclude only tentatively from Figure 16 that the particle size distribution in FBC is not radically different from a conventional system, although there could be more fine particles in atmospheric FBC emissions. The FBC data should be considered tentative because it is taken from relatively small test systems compared with the size of conventional systems.

Particulate mass emissions reaching the final control device of a FBC system will probably be lower than in a conventional system. However, this concentration will depend on both the amount and size distribution of the particulates reaching the cyclone precollectors as well as the design of those precollectors. The amount of fine particulates reaching the cyclones can only be determined experimentally, and care should be exercised to distinguish between particle mass and particle number. The design plan for the Pope, Evans and Robbins - FBC system indicates an expected mass concentration of 0.7 grains/ft^3 reaching the final control device.[10] Particulate emissions reaching the final control device in a conventional system are higher - typically 2 to 3 grains/ft^3.

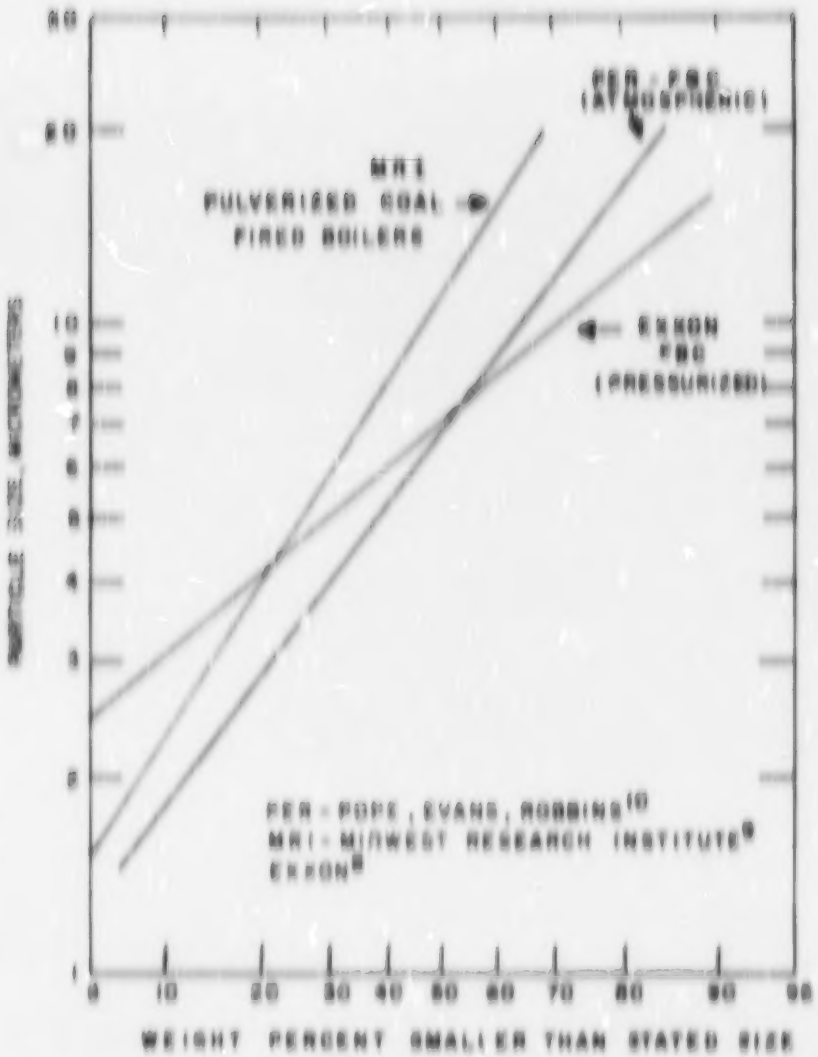

Figure 16. Particle size distribution before final control device

The concentration of SO_2, SO_3 and water vapor in the flue gases can also affect the selection of particulate control equipment. Water in flue gases from combustion is primarily a result of the fuel hydrogen content and it produces a dew point of 50 to 65°C at normal excess air. However, as illustrated in Figure 17, the SO_3 concentration (usually 1 to 2 percent of the SO_2 concentration) in a conventional coal-fired boiler raises the flue gas dew point.[11] Equipment designed to collect dry particulate (fabric filters and dry electrostatic precipitators) must operate above the acid dew point. Most conventional coal-fired plants maintain flue gas temperatures between 150 and 180°C to avoid corrosion problems. Robinson et al.[12] found that the Pope, Evans and Robbins - PER system produced an SO_3 concentration of 39 ppm when sorbent was not used, and no measurable SO_3 when sorbent was used. (Note: These early SO_3 results represent limited data and must be confirmed by further SO_3 analyses on other fluidized bed combustors.) Such a very low SO_3 concentration in the presence of sorbent, if confirmed, means that flue gases might be cooled to 95°C or below for dry particulate collection and increased heat recovery. The major problem in using fabric filters on coal-fired boilers has been SO_3 and H_2SO_4 induced deterioration of the fabric. Therefore, fabric filter technology may also be readily applicable to fluidized bed combustion systems if the low SO_3 concentrations are confirmed.

The concentration of SO_3 and the acid dew point will also affect the performance of electrostatic precipitators. Burning low sulfur western coal has resulted in decreased electrostatic precipitator performance, and SO_3 has been added to the flue gas as a conditioning agent.[13]

Electrostatic Precipitators - An electrostatic precipitator can be applied before or after the final flue gas heat recovery unit as previously illustrated in Figure 16. In the design of the Pope, Evans and Robbins 30-MW demonstration plant, an electrostatic precipitator was selected to operate at 315 to 370°C before the final heat recovery (a hot side precipitator) because of the high resistivity of the particulates at low temperatures.[10] Therefore, the unit must handle a larger gas volume than if low

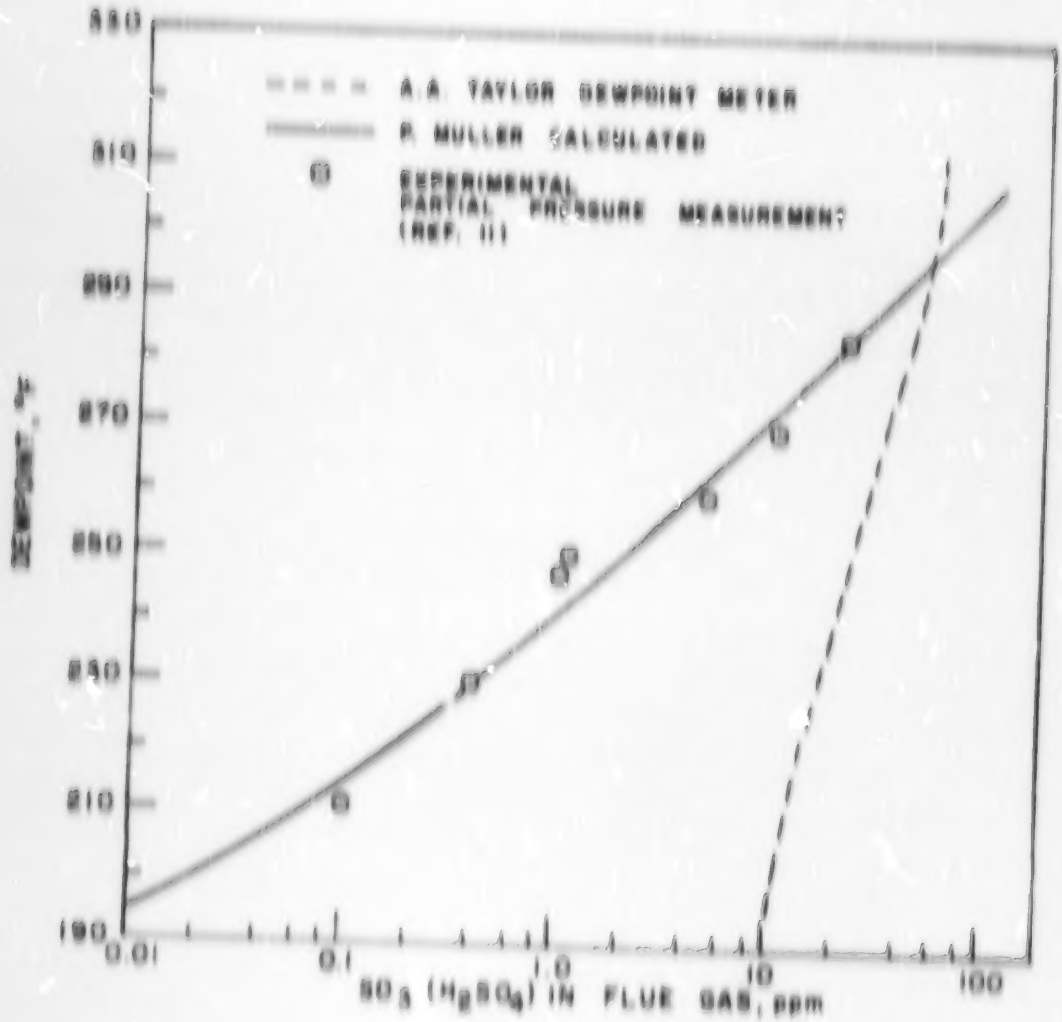

Figure 17. Dew point elevation as a function of SO_3 concentration[11]

temperature operation were possible. With good design and operation, hot side electrostatic precipitation can collect fine particulates at high efficiencies as illustrated in Figure 18.[14] Similar performance can be attained with cold side precipitation when the aerosol properties are suitable. However, there have been some problems in designing precipitators to operate at high efficiencies. Data published by Benson and Corn[15] show that among 14 large electrostatic precipitators, having an average design efficiency of 98.2 percent, the actual average operating efficiency was only 89.0 percent. Accurate data on particle size distribution, mass concentration, and in situ resistivity are needed for proper electrostatic precipitator design for FBC systems. Designing precipitators for FBC systems based on analogies with previous operating experience in conventional combustion systems can be very risky. There have been many examples of precipitators designed to operated at 95 to 99 percent efficiency which actually operated at 50 to 90 percent efficiency.[16]

Electrostatic precipitators have been very widely accepted by the utility industry because they have been applied over many years with minimal maintenance problems. However, the size and capital cost rise sharply as design efficiencies are increased to 99 percent and above. Fly ash resistivity is a very important factor in ESP performance and may need more study with respect to fluidized bed combustion. However, methods to combat resistivity problems are being studied, including the use of hot side precipitators, and fly ash conditioning with SO_3, ammonia, and sulfamic acid. If resistivity problems require operating temperatures of 370°C instead of 95 to 150°C, then many normally condensable organics and condensable trace metal compounds will not be collected. Nevertheless, one significant advantage of electrostatic precipitators is that the power requirements are lower than other control devices.

Wet Scrubbers - Most wet scrubbers that are commonly used collect particulates primarily through inertial mechanisms and thus require large amounts of power to collect fine particulates at high efficiencies. Venturi scrubbers are used with very high pressure drops to collect fine

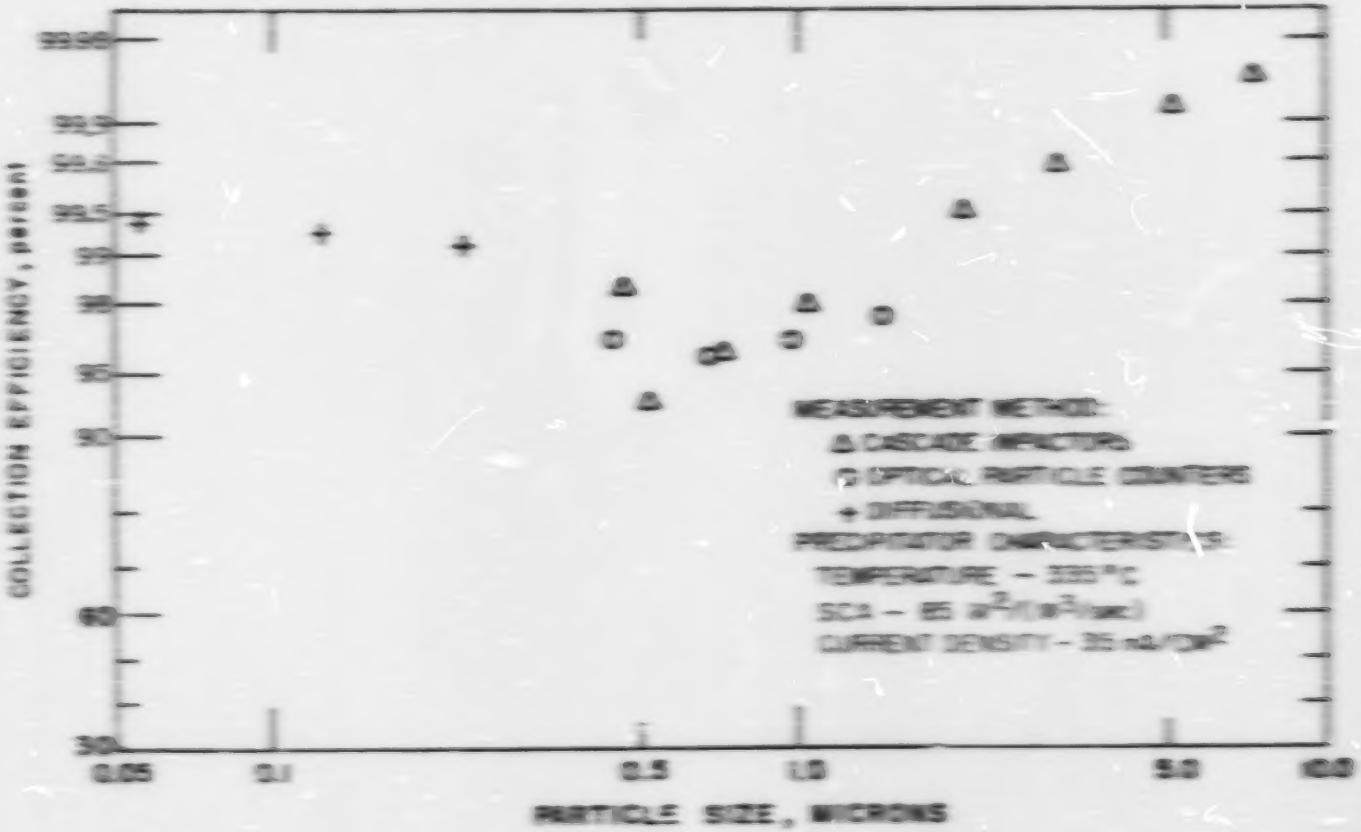

Figure 38. Measured fractional efficiencies for a hot side electrostatic precipitator, with the operating parameters as indicated, installed on a pulverized coal boiler[34]

particulates. Figure 19 presents calculated particle penetrations for a venturi scrubber as a function of pressure drop, particle size, and f factor. The f factor is an empirically determined constant and is a function of particle wettability, venturi throat liquid distribution, and other factors.[17] Figure 19 shows that for an f factor of 0.25, a 98 percent collection efficiency for 2-micron particles requires a pressure drop of 8 inches of H_2O. To collect 1.0- and 0.5-micron particles at the same collection efficiency and same f factor, pressure drops of 33 and 135 inches of H_2O, respectively, are required. Clearly the performance of a scrubber decreases sharply as the particle size decreases.

Wet scrubbers present certain advantages when used on an FBC system. They typically operate at the water saturation temperature of the gas (below 95°C); therefore, organic compounds and volatile trace metal compounds could be condensed and separated from the flue gas. By scrubbing with an alkaline solution, acid gases such as HCl could be collected, if necessary.

The disadvantages of a wet scrubber for FBC systems, however, appear to be severe. To achieve high efficiencies, present designs require very large pressure drops and thus high power consumption and operating costs. Disposal of the scrubber water may create a potential water pollution problem. In addition, stack gases must usually be reheated (an expensive operation) to avoid plume formation.

Fabric Filters - Only recently have fabric filters been used on conventional coal-fired utility boilers because of the questionable life span of fabrics exposed to SO_2, SO_3 and moist flue gases. Of the filter materials commonly used, glass fabrics are the most acid resistant and the most cost competitive. The very low SO_2 concentration and the apparently small amount of SO_3 in the flue gases of an FBC system may provide the impetus for the use of fabric filters. Moderately acid resistant fabrics[18] such as NOMEX, orlon, and dacron can be used. A fabric filter would necessarily be used after the final heat recovery unit.

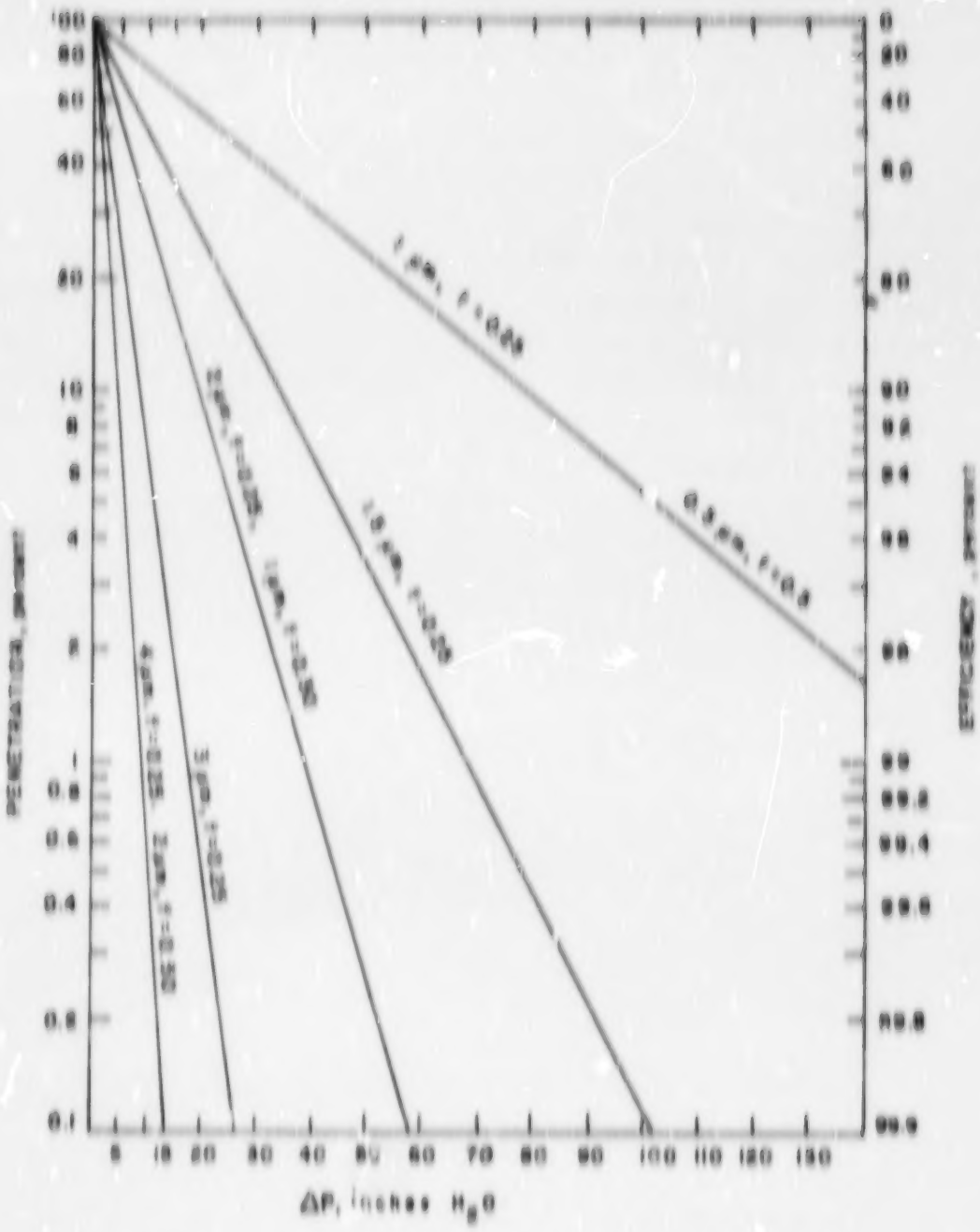

Figure 19. Penetration calculated from a venturi scrubber model as a function of pressure drop and particle aerodynamic diameter[17]

The possibility of operating at temperatures near 95°C (as acid dew point elevation is not a factor) also favors a fabric filter control device.

The fractional efficiency of a fabric filter installed on a coal-fired boiler in Nucla, Colorado, is shown in Figure 20.[4] Although there was considerable scatter in the original data, efficiencies for particles 1 to 10 μm diameter were high, ranging from 99.4 to 99.8 percent. Similar test data for a boiler burning pulverized anthracite showed higher efficiencies, ranging from 99.75 to 99.87 percent in the 1 to 10 μm range.[5] Overall mass efficiencies at the two test sites were 99.8 and 99.9 percent over test periods of a couple of months. The bags at the Sunbury steam station had been in use for 2 years when the field test was conducted.

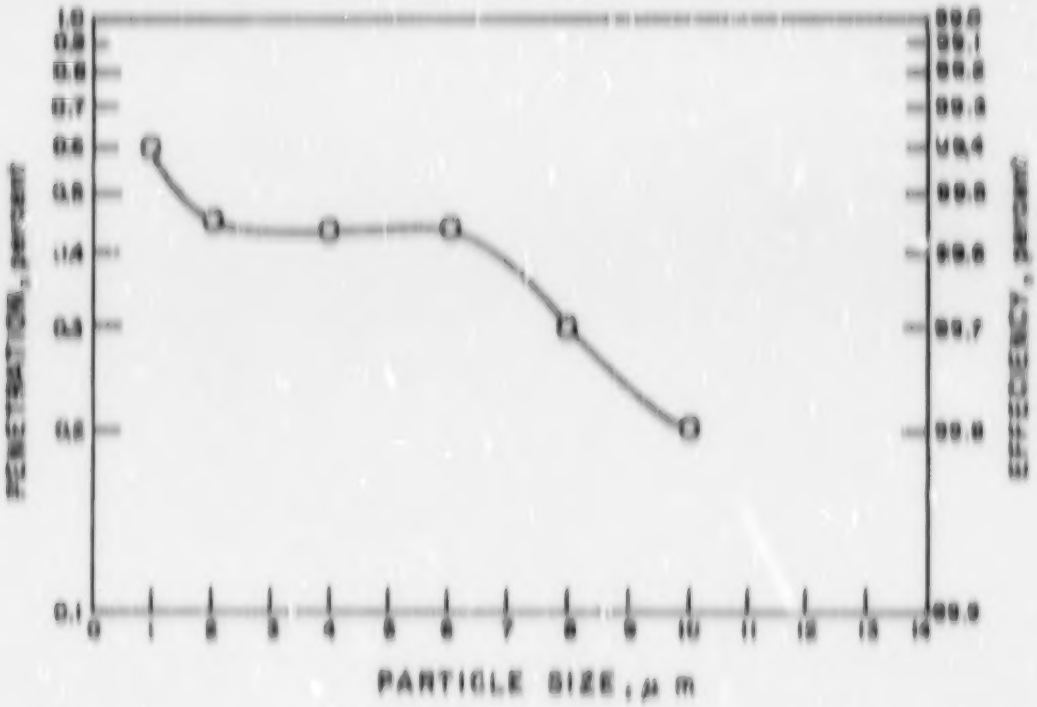

Figure 20. Median fractional collection efficiency for 32 tests[4]

Fabric filters have several advantages over other control systems. Collection efficiency does not depend on particle resistivity. Very high efficiencies of 99.5 to 99.9 percent for fine particulates can be routinely achieved by fabric filters. These efficiencies are out of the range of venturi scrubbers and can only be achieved by ESP through enlarged precipitators and sharply increased costs.

One disadvantage of suggesting fabric filters for particulate control in FBC systems is that fabric filters have only recently been used on utility boilers and some operators may doubt their reliability and may be unwilling to use them.

Particulate Control for Pressurized Combustion Systems

There are two pressurized FBC systems under consideration. One operates at 15 to 25 percent excess air, while the other, the adiabatic system, operates at 300 percent excess air. Because the cost of large scale particulate control equipment is proportional to the actual gas volume handled, the capital and operating cost of particulate control equipment for an adiabatic system would be approximately triple the cost for a normal excess air system to achieve the same number of $lb/10^6$ Btu of emissions.

Control devices for pressurized fluidized bed systems should operate at high temperature as well as high pressure if placed upstream of the gas turbine, in order to maximize energy recovery from the turbine. A particulate control system operating at 800°C would fail to collect condensable materials in the flue gas that could be collected at temperatures of 375°C by hot electrostatic precipitators or at 95 to 150°C by other control devices. Thus, it may be necessary to place a control device for particulates or other pollutants in the low temperature ducting downstream of the gas turbine in order to meet environmental requirements.

Particulate control equipment for high temperature and pressure operation is not yet commercially available and considerable development is required before any such equipment will be available.[19] The problem of controlling particulates at high temperature had led to a preliminary review of concepts for cooling, cleaning, and reheating the flue gases before application of the gas turbine.[20] Table 30 is a summary of potential high temperature particulate removal systems. Molten salt scrubbers cannot be applied to pressurized FBC systems because the alkali metal vapors would cause gas turbine corrosion.

The Aerodyne Tornado cyclone has been seriously considered for application of FBC systems. Figure 21 depicts the operation of the Aerodyne Tornado cyclone which is claimed to have unusually good collection efficiency for fine particulates compared to conventional cyclones.[19] It appears unlikely, however, that cyclones -- even of advanced design -- will be able to achieve the high efficiencies for fine particulates that may be needed for operation in the mid 1980's era. Some type of device in addition to cyclones will be needed even to meet the current New Source Performance Standards for particulates from large coal boilers.

Electrostatic precipitators could encounter severe operating problems at high temperatures and pressures, particularly in maintaining stable coronas.

Fabric filters are also an option for high pressure operation, but there is still a great deal of development work needed. A basic problem is the need for a fabric capable of maintaining its physical integrity under fabric filter cleaning procedures, hence there is now considerable research underway to develop "advanced" fibers. Some of the most efficient fabrics are composed of very fine fibers similar to Brunswick Metal fibers (~ 8 to 12 microns in diameter). However, corrosion and oxidation of these metals is greatly enhanced at high temperatures.

Table 31. [illegible]

Device	Developer	Operating conditions: Typical, °C/psi	Operating conditions: Range, °C/psi	Corrosion control efficiency for H_2S + CO_2	Potential for solid removal	Energy sensitivity/ operating costs	Potential operating problems	Comments
I. Sorbents		[illegible]	[illegible]	Low	None	Low/Moderate	Low	Adequate experience in operation in the presence of H_2S. The sorbent technology is well developed.
• Amine Treating Systems	Amine Development Corporation	[illegible]	[illegible]	Moderate	None	Moderate/High	Low/Moderate	Corrosion and requirements and performance at high temperature and pressure should be investigated.
• Selexol Process	Allied Chemical	[illegible]						
II. Wet/Dry Scrubbers		[illegible]	[illegible]	High	High	Moderate	Moderate	Adequate experience in Europe/Asia in the petroleum, chemical, metals and gas separation. Theoretical and experimental studies are limited. Needs further study in the removal efficiencies and costs.
	Combustion Power	[illegible]						
	Exxon	[illegible]						
	Lurgi/Ruhrchemie	[illegible]						
	Rockwell	[illegible]						
	Rockwell, CPU	[illegible]						
III. Electrostatic precipitators		[illegible]	[illegible]	High	None	Low	High	Extensive experience in industrial, chemical, and gas separation. Some considerable development work before reliable data can be developed. Removals of submicrons, aerosols, and fumes under a variety of conditions are under studies.
IV. Filters and membranes		[illegible]	[illegible]	High	High	Moderate	Moderate	Particulate entrainment over additional cleaning problems. The removal for gas-solids removal and electrostatic may be important in some applications.
	Research Triangle Institute							
	Monsanto Research Corporation							
V. Hybrid Systems		[illegible]	[illegible]	High	Low	Low	Moderate	Needs considerable development work. Solid removal, ionic life, removal of collected material, and other basic information problems have to be investigated.
• Venturi-Fabric Filter	U.S. Bureau of Mines	[illegible]						
• Venturi-Fabric Filter	TVA Division	[illegible]						
• Wet Cyclone	Research Corporation	[illegible]						
VI. Other Wet, Dry, and Fabric Filters	[Data not yet available for inclusion in this report.]							

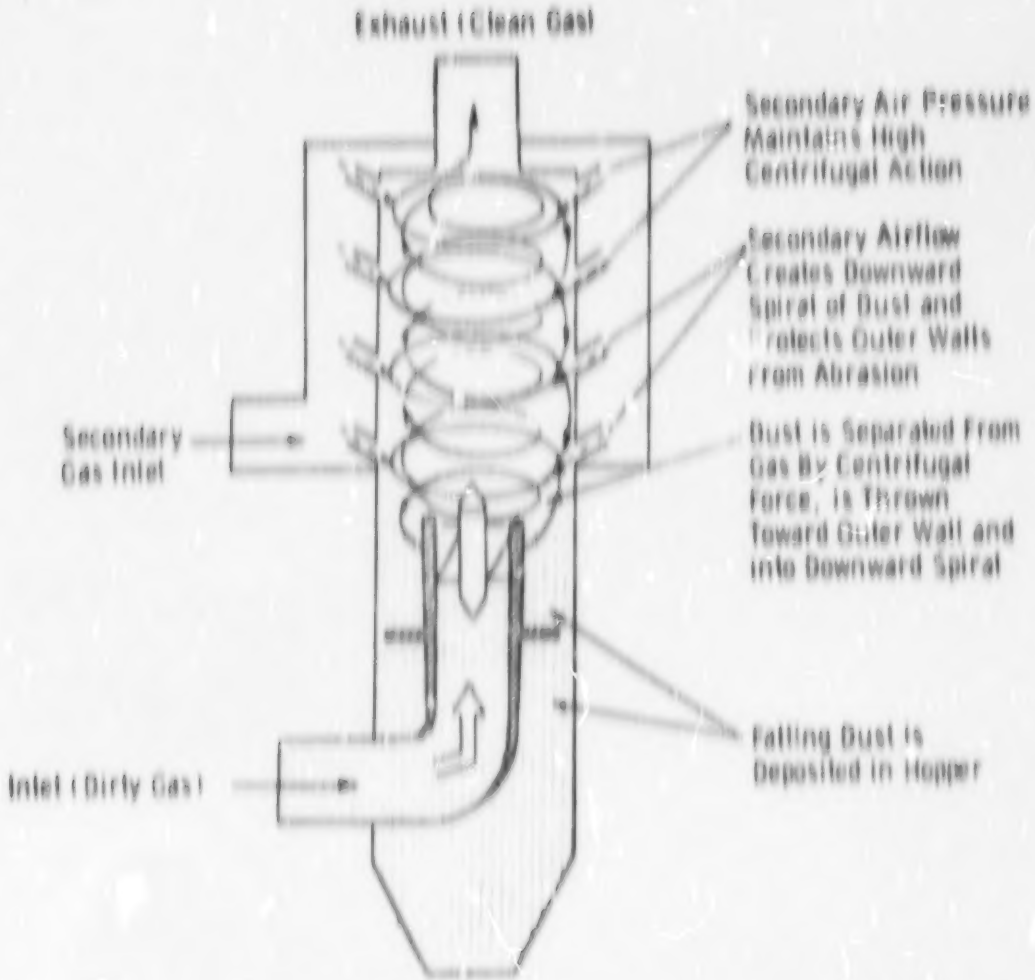
Exhaust (Clean Gas)
Secondary Air Pressure Maintains High Centrifugal Action
Secondary Airflow Creates Downward Spiral of Dust and Protects Outer Walls from Abrasion
Secondary Gas Inlet
Dust is Separated From Gas By Centrifugal Force, is Thrown Toward Outer Wall and into Downward Spiral
Falling Dust is Deposited in Hopper
Inlet (Dirty Gas)

Figure 21. Schematic representation of Aerodyne particulate separator[19]

Gravel bed filter technology is promising, but further development is also needed here. Exxon is in the process of acquiring a Ducon granular bed filter for their FBC miniplant.[21] The filter should be placed in operation during 1976. Data on gravel filters are very limited, and the results of the Exxon studies will be needed for a reasonably accurate assessment of particulate control efficiency.

Control of Gaseous Emissions

Some of the gases (other than SO_x and NO_x) which could be present in quantities possibly high enough (e.g. > 10 ppm) to require some sort of control measures include: HCl, CO, unburned hydrocarbons (HC), and possibly COS. Each is discussed briefly below.

HCl - HCl could be troublesome, especially if NaCl is used to enhance SO_2 sorbent performance as proposed by some workers. It could also be a problem with high chlorine content coals. Aside from restricting the use of the above materials, the best control option for HCl seems to be scrubbing with an alkaline spray. Such sprays are sometimes used in solid waste incinerators; candidate scrubbing solutions are carbonates and bicarbonates. For maximum economy, the spray device would also have to be useful for particulate removal (as discussed more fully in the previous section).

CO - High CO levels should not be routinely encountered based on available data from existing FBC units. High CO levels, if they do occur, should be able to be brought under control by increasing the extent of combustion within the burner. This can be accomplished in several ways: increasing excess air, increasing bed residence time, or by addition of secondary air. The choice between these options is not necessarily straightforward and will depend on the economics and design features of specific units.

Hydrocarbons - Hydrocarbons (HC) are also products of incomplete combustion and their emissions should be able to be reduced by the same techniques listed above for CO. Studies on HC levels as a function of excess air indicate very low emissions (< 50 ppm) provided excess air levels are kept above 15 to 20 percent. Should special circumstances warrant air levels below 20 percent, one also has the option of collecting some of these compounds as particulates after cooling the flue gas. Most of the high molecular weight compounds (especially polycyclic compounds) condense below 315°C.

COS - COS emissions could conceivably be a problem; if present, COS can be removed via conventional H_2S scrubbing techniques such as the Rectisol process (a methanol scrubbing solution at -55°C), but these are not practical for combustion gases. Alternate control methods, such as catalytic destruction, should be investigated. Zinc oxide is very effective in removing trace quantities of sulfur compounds from hydrocarbon gases at high temperature. Treatment with zinc oxide in the temperature range 315 to 425°C can produce a product gas having less than 0.1 ppm sulfur, as COS, H_2S, or CS_2.[22]

POLLUTION CONTROL VIA PROCESS MODIFICATIONS: SOME CONSIDERATION BASED UPON FLUIDIZATION FUNDAMENTALS

The following design and operating parameters can influence pollutant formation in fluidised bed combustion:

- Bed depth
- Bed and boiler tube geometry
- Fluidising grid design
- Particle size
- Fluidisation velocity
- Excess air
- Mechanism of coal injection
- Pressure.

Most of the above factors are interrelated; e.g., fluidization velocity and bed geometry affect the quality of fluidization, thus affecting gas-solid contact, heat transfer, and temperature distribution. The purpose here is to discuss the manner in which these parameters may affect pollutant formation. This information can then possibly serve as a starting point for pollution control via modification of appropriate process parameters.

It is important to note that much of the discussion here is based on existing models for low temperature fluidized bed systems. There may be difficulties in extrapolating some of the conclusions to the higher temperature regime of combustion; nevertheless, the discussion provides a useful starting point for considering some basic problems.

Bed Depth

Bed depth will influence gas residence time, bed pressure drop, and the quality of fluidization. Its most important influence on pollutant formation, if any, will probably be in terms of its effect on the residence time of gas within the bed. Kunii[23] has indicated the fraction of gas bypassing the bed decreases as bed depth is increased and attributed this to increases in the gas residence time. Because a bubble remains in the bed for a longer time as the bed depth is increased, it has more time in which to interchange gas with the emulsion phase. As gas exchange increases, bypassing is reduced. Increased gas exchange, should increase combustion; hence, it should tend to reduce the formation of compounds such as CO and unburned hydrocarbons. Increased gas exchange will enhance in situ capture of SO_2.

As mentioned above, bed depth will also affect the quality of fluidization. Poor fluidization, such as slugging or bubbling, can increase particle elutriation and emissions of unburned hydrocarbons. According to the relationship of Broadhurst and Becker[24] the minimum slugging

velocity varies inversely as the bed height to 0.9 power for settled bed-height to diameter ratios less than 3. For height to diameter ratios greater than 3, Steward predicts the minimum slugging velocity will be independent of bed height.[25]

Bed and Boiler Tube Geometry

Bed diameter and boiler tube configuration can influence gas mixing, slugging characteristics, and bubble flow. Zenz and Othmer report a twentyfold increase in mixing length (or intensity of mixing) due to an increase in diameter from 1 to 6 inches.[26] An approximately equivalent effect on eddy diffusivity was noted when diameter increased from 6 to 18 inches. Studies by the National Coal Board (London), however, have shown that bed cross-sectional geometry had little effect on their results.[27] The effect of geometry most likely will vary from unit to unit; but, in general, the quality of fluidisation increases with increasing bed diameter, which is encouraging since it implies that full-scale units may be better behaved than their bench-scale predecessors as far as potential pollutant generation via phenomena such as bypassing or elutriation are concerned.

The boiler tubes can serve to break up bubbles, providing smoother fluidisation. However, if they are too densely packed, the tubes can prevent good mixing in the bed. The influence of boiler tube configuration on solids-gas mixing (or quality of fluidization) was observed by Esson Research and Engineering.[28] They noticed flatter temperature profiles, an indication of good mixing, when the tubes were oriented vertically rather than horizontally. The configuration of the boiler tubes could present a problem in scale-up. Tube spacing, pitch, and size affect the mixing characteristics in the bed and thus affect the temperature profile.[29] Packing tubes too closely will cause large temperature gradients.

Esson noted channeling after installing vertical tube bundles.[28] Upon examination of their tubes, they noticed distinct areas of corrosion.

This was attributed to impingement of high velocity gas (channels). They indicated, however, that channeling could be eliminated by proper design and operation.

Fluidizing Grid Design

Grid design is an extremely important factor in providing good fluidization. Unevenly distributed gas can cause channeling and subsequent deactivation of portions of the bed, causing potential release of substances such as SO_2, NO_x and hydrocarbons. It is generally recommended that the grid pressure drop be 40 percent of the bed pressure drop to ensure uniform distribution. A better quality fluidization can also be obtained by decreasing hole size and increasing their number.[30] The effect of grid design is illustrated in Figure 22.[31] Sintered plate distributors, although providing the best fluidization, are generally not used in large commercial operations because of their fragility. However, the combination of a sintered disk and a sturdy support presents an attractive option. Bottom has found that a large portion of the chemical reactions occurring in a fluidized bed takes place in the grid region.[32] Between 30 and 50 percent of the fast first order reaction which he studied took place in that zone. Cooke et al. noticed a rapid reaction between oxygen and coal in the first 9 inches of a fluidized bed carbonizer and very little above this height.[33] Rehle and Kehoe also found the grid zone to be of major importance for fast reactions.[34] Several studies have shown that NO formation in fluidized beds occurs mainly near the distributor.[35,36] Very little additional chemical change occurs in the rest of the bed. Accordingly, changes in operating variables such as fuel/air ratio, which affect the chemistry in the distributor zone, strongly influence the combustion chemistry; hence, this magnifies the importance of grid design.

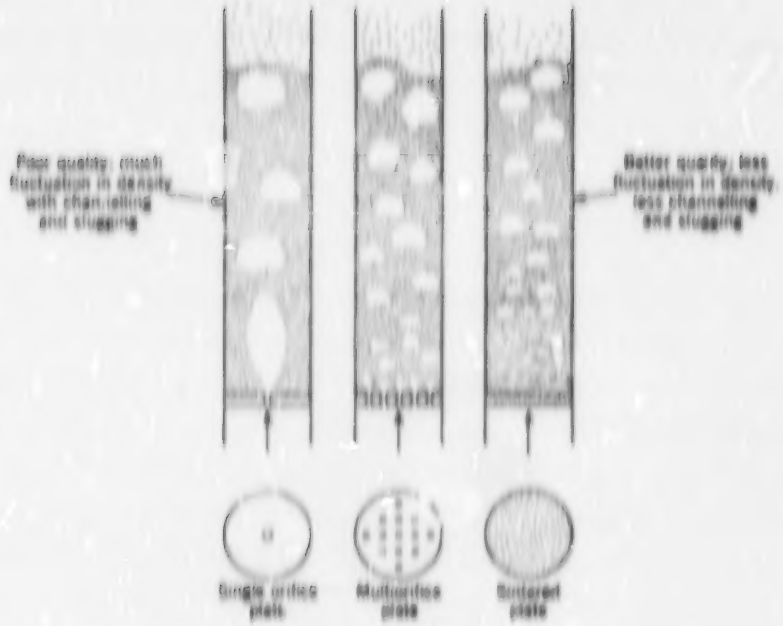
Poor quality; much fluctuation in density with channelling and slugging
Better quality; less fluctuation in density, less channelling and slugging
Single orifice plate
Multiorifice plate
Sintered plate

Figure 22. Quality of fluidisation as influenced by type of gas distributor[31]

Particle Size

The particle size distribution within the bed can influence not only the physical characteristics but also the chemical nature of the bed. It will influence the velocity needed for fluidisation, the height of the dense and dilute phases, elutriation, the quality of mixing, combustion, and channeling and slugging phenomena. The size distribution may thus affect emissions of SO_2, NO_x and hydrocarbons.

In general, the quality of fluidisation is better for smaller average particle sizes and larger particle size distributions. For high performance chemical reactors (reactors not necessarily designed for combustion reactions), the optimum diameter ratio of the largest to smallest particle should be between 12 and 21.[17]

Elutriation is a function of both velocity and particle size. If the fluidizing gas travels above the terminal velocity of a given particle, any decrease in size of the particle will cause it to be carried out of the bed. This is assuming that there is no particle/particle interaction which would cause the minimum fluidization velocity to differ from the particle's terminal velocity. Due to the complex nature of a fluidized system, however, particles whose terminal velocities are greater than the fluidizing velocity can be carried out of the bed. (A further description of elutriation is presented later in this section.)

Vogel et al. studied the effect of coal feed particle size on SO_2 retention.[38] They observed similar retentions (about 78 percent) for coal feeds ground to -12, 450, -80, and -16 mesh. Retention was found to be better (81 percent) for the coarsest feed. They also found that additive particle size had only a moderate effect on sulfur retention.

Wright has found that decreasing limestone size increases SO_2 reduction.[27] A similar decrease in dolomite size had no effect on SO_2 reduction, which suggested that access to internal surface was not a limiting factor for dolomite. An additive too finely ground may have too short a residence time to achieve a high degree of SO_2 removal. Thus, at high velocity, the effect of increased surface area may be counteracted by a decrease in residence time. Data obtained from British Studies support this claim.[27]

As mentioned earlier, particle size will influence phenomena such as bubbling, slugging, and channeling. The minimum slugging height is predicted to change with the -0.4 power of particle diameter.[39] The velocity at incipient slugging increases as the square root of particle diameter for height to diameter ratios less than 3. For height to diameter ratios greater than 3, the minimum slugging velocity increases with an increase in minimum fluidizing velocity (and thus particle size).

Fluidisation Velocity

The fluidisation velocity will influence gas and particle residence time, quality of fluidisation, elutriation, temperature distribution, and chemistry. The quantity, size, and velocity of bubbles, as well as the amount of gas bypassing as bubbles, is influenced by the superficial velocity. (The fluidisation velocity is often expressed in terms of the superficial velocity, which is the velocity the fluid would have if the reaction chamber were empty.)

The fluid residence time can be easily determined if plug flow conditions are assumed and the volumetric flow rate and free volume (total volume less particle and tube volume) are known. However, due to the turbulent nature of fluidized bed, a great deal of backmixing occurs. Also, bubbles pass through the bed at velocities greater than those of the fluid in the emulsion phase. The fluid, therefore, cannot be characterized by a single residence time. In the absence of residence time distribution data, a residence time could be calculated for each phase within the bed; i.e., emulsion, bubble, and dilute. In the case of the emulsion and dilute phases, the residence time can be found by dividing the height of the phase by actual velocity (superficial velocity/void fraction). Bubble residence time can be calculated in the same manner; however, the bubble velocity must be known. Davidson and Harrison have presented a relation to determine bubble velocity as a function of bubble diameter and superficial and minimum fluidising velocities.[40] In the absence of any other information, the maximum stable bubble diameter can be used to determine the bubble velocity. The maximum stable bubble diameter can be found from knowledge of particle size, particle density, and fluid density.[40] In general, an increase in velocity causes a corresponding decrease in residence time.

In some pilot plant experiments, it has been noted that by increasing the superficial velocity, the primary combustion zone moved from an

area near the coal injection point to a zone near the top of the bed.[39] Increasing the velocity also had the effect of slightly increasing temperatures within the bed (presumably because increased velocity also meant an increase in excess air; hence, better combustion).

Estimating the fraction of gas bypassing the bed is a relatively simple procedure if the bubble velocity and size are known. Relationships have been developed for calculating both bubble velocity and bubble size.[40,41] However, experimental verifications of these models were performed under conditions very dissimilar to those in a fluidized bed coal combustion unit. Hence, although methods are available for estimating the maximum stable bubble size, which in turn could be used to determine the fraction of gas bypassing, the results at best should be viewed as upper limits. Studies of heat transfer coefficients in fluidized beds indicate that the fraction of gas bypassing can sometimes range between 40 and 70 percent.

The extent of gas and solid mixing is also affected by superficial velocity. Internal solids circulation is extremely rapid and increases with velocity. During experiments in a 5-foot diameter, 32-foot deep bed of catalysts fluidized at 0.8 fps to determine mixing rates, it was found that 50 grams of powder was essentially completely mixed into 15 tons of powder in less than 1 minute.[42]

Excess Air

The amount of excess air will have a direct effect on the chemistry of the bed; a change in excess air will also affect the bed's physical properties indirectly at a given coal feed rate by changing the superficial velocity, the effects of which have been discussed previously. The effect of excess air on SO_2 reduction with limestone, at constant superficial velocity, has been studied at Argonne National Laboratories. Sulfur reduction

increased from 67 to 75 percent when the oxygen level in the flue gas increased from 0.7 to 5.6 percent, which corresponds approximately to an increase in excess air from 5 to 35 percent. (As discussed previously in Section III, total hydrocarbon emissions can be reduced to less than 50 ppm provided excess air levels of 15 to 20 percent are maintained.)

An increase in excess air increases the amount of energy leaving the combustor as the sensible heat of the off gases. At low levels, this increase is compensated by the increase in combustion efficiency. At higher levels, however, the heat removed by the flue gases exceeds that produced by higher combustion efficiencies. To maintain constant bed temperature, some heat transfer surface must be removed. If this is not possible, the bed temperature will drop. Increasing excess air levels even further (to about 300 percent) will result in a situation where all the heat transfer surface must be removed to maintain a constant bed temperature. At this point, the bed becomes an adiabatic combustor. Any increase beyond this point will lower the bed temperature.

The elutriation rate from a fluidized bed will determine the load on any particle collection equipment (cyclones) and also the amount of particulate emissions. It is affected by such factors as particle size distribution, particle density, bed cross section, and terminal and superficial velocity.

The entrainment rate decreases as freeboard height increases. If the height is increased sufficiently, a height will be reached at which the entrainment rate is constant. This height is termed the transport disengaging height (TDH) and is defined as the point at which steady flow conditions are established.

Merrick and Highley have developed both an analytical and numerical model for particle size reduction and elutriation for a fluidized bed process.[44]

Data to obtain empirical constants for their relation were taken from the results of the British Coal Utilization Research Authority's 3- by 3-foot combustor.

Mechanism of Coal Injection

The manner in which coal is injected into the bed has an effect on combustion efficiency, temperature distribution, and particle residence time. In some experiments with their batch combustor, Exxon Research and Engineering noted burning in the freeboard zone.[28] Although velocity also had an effect on the degree of combustion in the freeboard, it was determined that the mechanism of coal feeding was the major source of the problem. Combustion above the bed was eliminated by changing the position and orientation of the coal feed probe from a position 2½ cm above the fluidizing grid and a 45° angle upward to a position just above the grid and a 45° angle downward. The observed combustion in the freeboard was attributed to a reduced particle residence time, resulting from the original coal feed orientation. Also of interest was the fact that no hot spots were observed with the new orientation.

Pressure

Pressure will influence gaseous equilibrium concentrations and will also influence the potential vaporization of various mineral compounds. Pressure will also influence the degree of slugging via fluid density changes.

For height to diameter ratios greater than 3, the minimum slugging velocity decreases with decreasing minimum fluidization velocity. Because the velocity at incipient fluidization decreases with increasing fluid density and thus pressure, the minimum slugging velocity should decrease with increasing pressure. Viscosity also changes with pressure; for a change in pressure from 1 to 10 atm, the velocity at incipient fluidization decreases by about 0.3 percent. Thus, the change in minimum slugging

velocity due to the contribution from the viscosity effects should be negligible for height to diameter ratios greater than 3. The minimum slugging velocity increases with pressure at values of height to diameter less than 3. A tenfold increase in pressure produces an increase in minimum slugging velocity of about 10 percent.

Pressure also has an effect on entrainment via fluid density changes. A tenfold increase in pressure causes approximately a tenfold increase in density (for gases). The terminal velocity of a particle decreases with increasing fluid density. Therefore, at constant superficial velocity an increase in pressure will cause larger particles to be elutriated. This effect is shown in Figure 23.[45]

CONTROL OF POLLUTANTS FROM SPENT STONE DISPOSAL

Solid waste could prove to be one of the most significant pollutants associated with fluidized bed combustion simply because of the potentially large quantities of waste produced by once-through sorbent operation. Table 21 presents estimates of the solid waste disposal requirements for a once-through fluidized bed combustion system as a function of the Ca/S mole ratio and the coal sulfur content.[46]

Table 21. SPENT BED PLUS ASH PRODUCED BY A 635-MW ONCE-THROUGH SORBENT FBC PLANT[a,46]
(10^3 tons/year)

	1% sulfur in coal	2% sulfur in coal	3% sulfur in coal	4% sulfur in coal
Ca/S = 2	300	433	569	704
Ca/S = 1.2	951	337	434	510

[a]Assumptions: Coal feed rate = 430,000 pounds per hour;
Ash content = 12 percent, 165 = 10^3 tons/year;
90 percent SO_2 removal;
73 percent load factor.

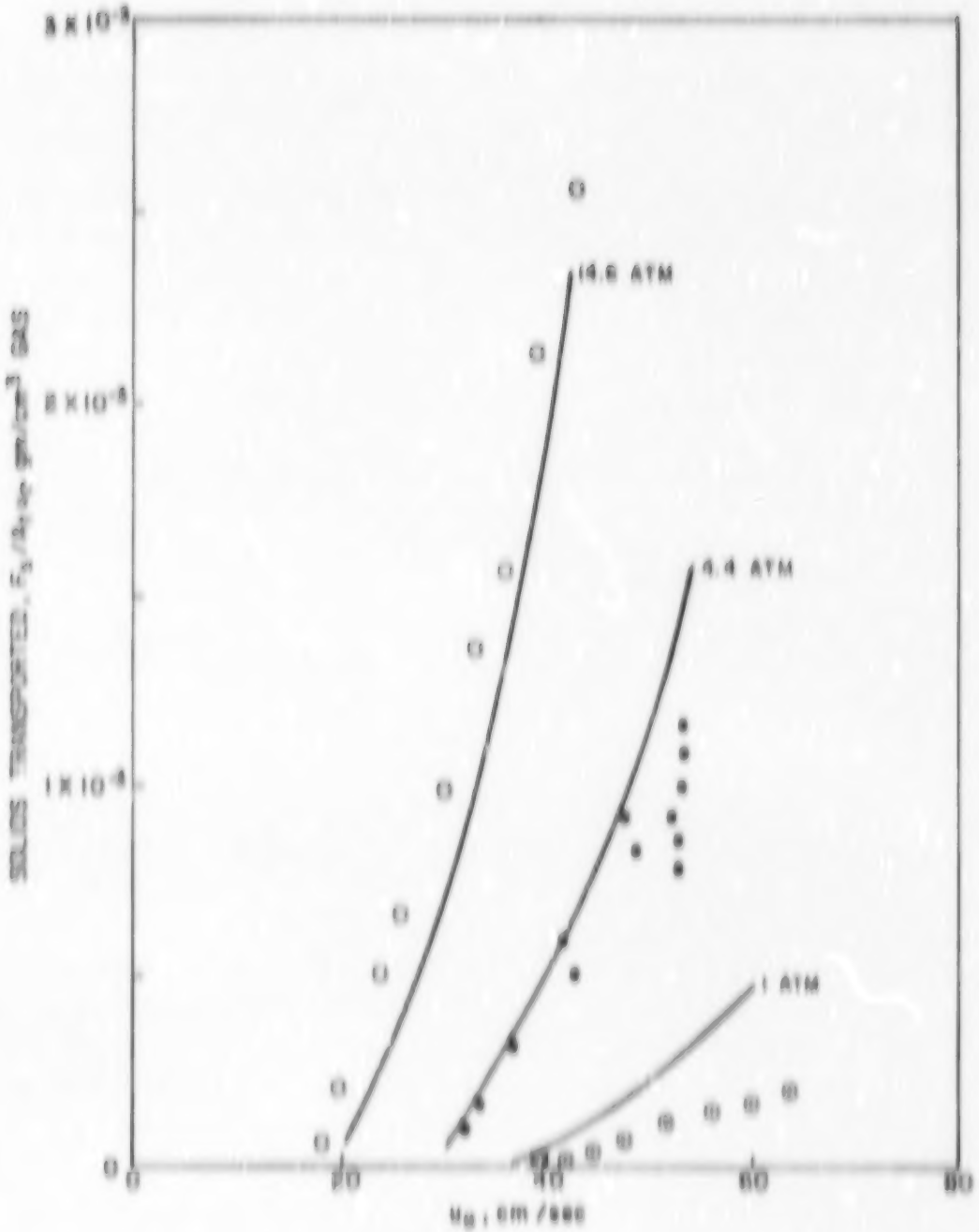

Figure 21. Comparison between calculated and experimental entrainment at various pressures[55] (solid lines are calculated)

The amount of solids produced at low Ca/S ratios would be similar to that from limestone scrubbing systems but the total mass of waste would be 50 percent less because the scrubber sludge contains 50 percent water while the FBC spent stone is dry.

Potential pollution from solid waste disposal includes leachates (trace elements and organic compounds) and possibly unsightly and large-scale land fills. As indicated earlier in Table 14 based on an assumed density of 100 lb/ft^3 (65 percent of the theoretical spent stone density), a 635-MW plant burning coal with 3 percent sulfur and 12 percent ash, and using a Ca/S ratio of 2, would require 260 acre-feet per year for spent stone disposal. Over a 30-year plant life, a landfill area of 260 acres would have to be 30 feet deep to accommodate this one plant.

Solid Waste Control Methods

The most effective method to reduce the volume of solid waste and the overall solid waste problem is to regenerate and recycle the sorbent. As previously discussed, several regeneration options are being actively investigated. Kearns et al. have found from laboratory thermogravimetric testing that the chemistry of regeneration appears to be favorable but cautioned that other factors such as attrition, coal-ash sorbent agglomeration, tar deposition on the sorbent or eutectic formation could limit the number of regeneration cycles in a commercial system.[47] Based on regeneration kinetics experiments, they suggest that 0.18 moles of Ca may effectively remove one mole of sulfur by being recycled 20 times. Therefore, compared to a once-through system, the solid waste burden attributable to sulfur removal would be reduced by 85 percent at a 1.2/1 ratio and by 91 percent if a 2/1 ratio were required for a once-through system.

Very little experimental information specific to FBC systems is available with respect to stone disposal or its utilization. However, some insight to the problem can be gained from a discussion of current methods for coal ash or scrubber sludge disposal. Due to its high water content

(over 50 percent), sludge from limestone scrubbing will almost always be ponded, either temporarily or permanently. Ponding presents the maximum potential for ground and surface water contamination, as large quantities of saturated water are present. Materials including PVC, Hypalon, concrete, clay, and asphalt are available for lining ponds to prevent groundwater pollution.[48] Most electric power plants transfer coal ash as a wet slurry for convenience and for the same reason wet transfer of spent FBC stone may be considered.

If disposal will occur via landfilling techniques, a landfill site should be selected and managed to minimize water pollution through leachates or surface runoff. Geological and hydrological evaluations are particularly important in selecting a site to minimize water pollution. Typical leachate migration rates range from 0.5 to 30 meters/yr and ground water pollution problems may take several years to develop.[49] Therefore, initial site selection and immediate pollutant monitoring are very important in developing new landfill sites and preventing difficult to correct future pollution problems. The landfill should be located above the natural water table and groundwater flows including springs should be rerouted around the landfill areas.[50]

A hydrogeological investigation is an essential part of selecting a landfill site in all areas.[50,51] Boring is required to obtain soil samples and determine water table levels.[52] The purpose of the survey is to determine the potential for leachates to reach the groundwater.

A general recommendation that landfills be located at least 3 to 10 feet above the water table is based on the natural containment concept. Natural containment depends on the ability of the soil to attenuate pollutants contained in the leachate. The best soils for pollutant attenuation, those which are fine grained; these are usually clays, silts or granular soils with high clay content.[50] Physical properties of soils meeting the requirements for natural attenuation are typically: permeability 10^{-6} cm/sec or less, at least 30 percent passing a 200 mesh sieve, a

liquid limit greater than 30 percent and a plasticity index greater than 15.[50] Mechanisms causing pollutant attenuation include dispersion, dilution, filtration, retention, ion exchange and biological breakdown. In a study of four landfills in Illinois it was observed that chlorides migrated farthest from the landfill site; similar results have been obtained by other investigators.[53,54] Soil attenuation of selenium and boron was reported to be poor.[55]

Semi-artificial containment can be accomplished by selecting a disposal site where extensive clay deposits are present and the soil is relatively impervious. Pond liners can be used to artificially contain leachate. In either case the leachate should be collected and treated with at least conventional water treatment techniques.[56]

Commercial Uses for Solid Waste By-Products

Commercial uses for the spent stone material are also being investigated. The major obstacles to using the spent stone will be the very large volumes generated (market saturation), transport costs and availability of competitive raw materials. As illustrated in Table 22, fly ash and bottom ash from conventional boilers are used in a number of products but only about 20 percent of the total is utilized.[57] This indicates that the market in this area for spent stone may be limited. New uses that have been considered for spent stone include autoclaved products - bricks, hot press sintering-pipes and metal coatings; gypsum products - wallboard and plaster; and mineral recovery. Gypsum from SO_2 scrubbing is used extensively in Japan,[58] but no large markets exist in the United States because of an abundant supply of natural deposits. Treatment of acid mine drainage is also a potential use for spent stone. Spent stone is also being considered as an agricultural supplement; pilot studies have shown successful application in peanut farming.

Table 33. ASH COLLECTION AND UTILIZATION, 1971[57]

	Fly ash, tons	Bottom ash, tons	Boiler slag (if separated from bottom ash), tons
Ash utilized:			
Mixed with raw material before forming cement clinker	104,222	NA	91,975
Mixed with cement clinker or mixed with cement (pozzolan cement)	16,536	NA	NA
Partial replacement of cement in:			
Concrete products	177,166	35,577	76,563
Structural concrete	185,467	NA	NA
Dams and other massive concrete	71,411	NA	NA
Lightweight aggregate	178,895	13,942	NA
Fill material for roads, construction sites, etc.	363,385	533,682	2,628,385
Stabilizer for road bases, parking areas, etc.	36,939	7,880	49,564
Filler in asphalt mix	147,655	2,833	81,700
Miscellaneous	98,802	475,417	428,026
Total ash utilized	1,380,478	1,069,131	3,356,713
Ash removed from plant site at no cost to utility but not covered in categories listed under Ash utilized	1,872,728	542,895	381,775
Ash removed to disposal areas at company expense	24,497,848	8,446,941	1,232,298
Total ash collected	27,751,054	10,058,967	4,970,786

NOTE: NA - Not applicable.

If stone regeneration is used, the final amount of spent stone might be reduced by 85 to 90 percent. In addition, a low sulfur (0.5 percent) lime product could be produced if the waste stone is bled out of the circulation loop after regeneration. This low sulfur lime product could sell for $20/ton, and at that price would be an economically attractive by-product.

Several projects funded by ERDA and by EPA are underway to investigate means for utilization of FBC solid residue. Among the larger utilization projects aimed specifically at FBC residues are two being funded by ERDA, one with the U.S. Department of Agriculture (agricultural uses) and one with IU Conversion Systems, Inc. (nonagricultural uses).

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APPENDIX

PRELIMINARY LIST OF CONCEIVABLE POLLUTANTS

Based on preliminary considerations of the prevailing temperatures and the chemical make-up of a coal-fired fluidized bed combustion system (coal, limestone, combustion or scrubbing additives, etc.), a list of potential pollutants has been prepared and is shown in Table 21.

This list is based on the major elements, C, H, O, S, N and the principal trace elements commonly found in American coals. The organic compounds (including sulfur and nitrogen compounds) are those which could result from incomplete combustion of coal. Only classes of organic compounds are listed since further detail would make the list too unwieldy. The trace element compounds are representative of species expected in the coal or limestone as well as in the combustion products. Chlorine compounds of these elements are included since, in some cases, NaCl is used to increase the efficiency of the sorbent bed.

Table 23. PRELIMINARY LIST OF POSSIBLE POLLUTANTS FROM FLUIDIZED BED COMBUSTION OF COAL.

ACIDS AND ACID ANHYDRIDES

1. Organic Acids
   a. Carboxylic acids: $R-\overset{O}{\overset{\|}{C}}-OH$ e.g., formic acid, benzoic acid, etc.
   b. Dicarboxylic acids: $HO-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}-OH$ e.g., phthalic acid, succinic acid
   c. Sulfonic acids: $R-\overset{O}{\overset{\|}{\underset{O}{\underset{\|}{S}}}}-OH$ e.g., benzenesulfonic acid

2. Inorganic Acids
   a. Sulfuric: H_2SO_4
   b. Sulfurous: H_2SO_3
   c. Nitric: HNO_3
   d. Nitrous: HNO_2
   e. Phosphoric: HPO_3
   f. Hydrofluoric: HF
   g. Hydrochloric: HCl

HALOCARBONS

1. Chlorinated Aliphatics: R - X e.g., chloromethane, chlorobenzene
2. Chlorinated Biphenyls:

Table 23 (continued). PRELIMINARY LIST OF POSSIBLE POLLUTANTS FROM FLUIDIZED BED COMBUSTION OF COAL

HYDROCARBONS

1. Alkynes: $-C\equiv C-$ e.g., acetylene, butyne, propyne, etc.

2. Diolefins: $-C=C-C=C-$ e.g., butadiene, pentadiene, octadiene, etc.

3. Olefins: $-C=C-$ e.g., ethylene, propylene, butene, etc.

4. Aromatics: e.g., benzene, toluene, etc.

5. Polynuclear Aromatics: e.g., anthracene, pyrene, phenanthrene, etc.

6. Cyclic Hydrocarbons: e.g., cyclopentane, cyclopentadiene, etc.

7. Aliphatic Hydrocarbons: e.g., methane, ethane, propane, etc.

NITROGEN COMPOUNDS

1. NO

2. NO_2

3. HCN

4. $(CN)_2$

5. NH_3

6. Amines: $R-N\begin{matrix}H\\H\end{matrix}$ e.g., methylamine, ethylamine, aniline, etc.

7. Pyridines: e.g., pyridine, quinoline

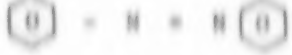
Table 23 (continued). PRELIMINARY LIST OF POSSIBLE POLLUTANTS FROM FLUIDIZED BED COMBUSTION OF COAL

8. Pyrroles:

9. Nitrate Salts: MNO_3 (where M is any cation)

10. Nitrite Salts: MNO_2 (where M is any cation)

11. Nitrosamines: R - N - N = O

12. Azoarenes: 

OXYGEN COMPOUNDS

1. Furan:

2. Ethers: R-O-R e.g., phenyl ether, anisole, etc.

3. Esters: e.g., phenylacetate, benzylacetate, etc.

4. Epoxides: e.g., ethylene oxide, propylene oxide, etc.

5. Alcohols: R-OH e.g., methanol, phenol, etc.

6. Aldehydes: e.g., formaldehyde, benzaldehyde, etc.

7. Ketones: e.g., acetone, benzophenone, acetophenone

PARTICULATES

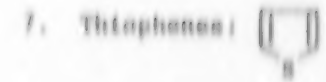
1. Size Distribution
   a. < 7 μm
   b. 2 μm < > 20 μm
   c. > 20 μm

Table 23 (continued). PRELIMINARY LIST OF POSSIBLE POLLUTANTS FROM FLUIDISED BED COMBUSTION OF COAL

RADIOACTIVE ISOTOPES

1. Uranium-233, Polonium-210, Lead-210, Radium-226, Bismuth-210, Thorium-227, Radon-222.

SULFUR COMPOUNDS

1. SO_2
2. SO_3
3. H_2S
4. COS
5. CS_2
6. S_n
7. Thiophenes: 
8. Mercaptans: R-SH e.g., methyl mercaptan, phenyl mercaptan
9. Sulfates: MSO_4 (where M is a metal ion) e.g., $FeSO_4$, $PbSO_4$, etc.
10. Sulfites: MSO_3 (where M is a metal ion) e.g., $CaSO_3$

TRACE ELEMENTS AND THEIR COMPOUNDS

1. Nickel: NiS, NiO, Ni_2O_3, $Ni(CO)_4$, $NiSO_4$, $NiCO_3$, $NiCl_2$, $Ni(CN)_2$, $Ni(OH)_2$
2. Cadmium: CdS, CdO, $CdSO_4$, $CdCO_3$, $Cd(CN)_2$, $CdCl_2$, $Cd(OH)_2$
3. Mercury: HgS, HgO, Hg_2O, $Hg(CN)_2$, $HgSO_4$, Hg_2SO_4, $HgCO_3$, HgCl, $HgCl_2$

Table 23 (continued). PRELIMINARY LIST OF POSSIBLE POLLUTANTS FROM FLUIDIZED BED COMBUSTION OF COAL

4.	Zinc:	ZnS, ZnO, ZnO_2, $Zn(SO)_4$, $ZnCO_3$, $ZnCl_2$, $Zn(CN)_2$, Zn_3N_2, $Zn(OH)_2$
5.	Lead:	PbS, PbO, Pb_2O_3, Pb_3O_4, PbO_2, $Pb(CN)_2$, $PbSO_4$, $PbCO_3$, $PbCl_2$, PbN_6, $Pb(OH)_2$, PbOH
6.	Sodium:	NaCl, Na_2O· Na_2SO_4, Na_2CO_3, $NaNH_2$, NaN_3, NaCN, NaH, Na_2O_2, $Na_2S_2O_7$, $Na_2S_4O_6$, $Na_2S_2O_3$, Na_2CS_3, Na_2SiO_3, $NaHSO_3$, $NaHSO_4$, $NaHCO_3$, NaOH
7.	Potassium:	KCl, K_2O, K_2SO_4, K_2CO_3, KCNO, KCN, KHS, $K_2S_2O_8$, K_2CS_3, $K_2S_2O_3$, $KHCO_3$, $KHSO_4$, $K_2Si_2O_5$, $K_2Si_4O_7$, KOH
8.	Vanadium:	V_2O_5, V_2O_3, V_2O_4, V_2S_3, $VOSO_4$, $K_2O \cdot V_2O_5$
9.	Cobalt:	CoS, Co_3O_4, CoO, Co_2O_3, $CoSO_4$, $CoCO_3$, $CoCl_2$, $Co(CO)_4$, $Co(CN)_2$, $Co(OH)_2$
10.	Molybdenum:	MoS_2, Mo_2O_3, MoO_3, $Mo(OH)_2$
11.	Copper:	CuS, Cu_2S, Cu_2O, CuO, $CuCO_3$, $CuSO_4$, CuCl, $CuCl_2$, CuCN, Cu_3N, CuOH, $Cu(OH)_2$
12.	Beryllium:	BeO, Be_2C, $Be(SO_4)_2$, $BeCO_3$, $BeCl_2$, BeH_2, Be_3N_2
13.	Selenium:	SeS_2, SeS, SeO_2, H_2SeO_3, H_2SeO_4, Se_2Cl_2, $SeCl_4$, $SeCl_2$
14.	Arsenic:	As_2S_5, As_2S_3, As_2S_2, As_2O_3, As_4O_6, H_3AsO_4, AsH_2, AsH_3, $AsCl_3$
15.	Antimony:	Sb_2S_3, Sb_2S_5, Sb_2O_3, Sb_2O_5, $Sb_2(SO_4)_3$, $SbCl_3$, $SbCl_5$, $Sb(OH)_3$
16	Fluorine:	F_2O_2, F_2O, F_2, NO_3F, HSO_3F, fluorinated hydrocarbons

Table 23 (continued). PRELIMINARY LIST OF POSSIBLE POLLUTANTS FROM FLUIDIZED BED COMBUSTION OF COAL.

17.	Chlorine:	Cl_2O, ClO_2, $HClO_3$, HCl, Cl_2, Cl_2O_7, $MClO_4$ (where M is a metal), chlorinated hydrocarbons
18.	Thallium:	Tl_2S, Tl_2O, Tl_2O_3, Tl_2SO_4, Tl_2CO_3, TlCl, TlOH
19.	Manganese:	MnS, MnS_2, Mn_2O_3, Mn_3O_4, MnO_2, $MnSO_4$, $MnCO_3$, $MnCl_2$, $Mn(CO)_5$, $MnSiO_3$, $Mn(OH)_2$
20.	Iron:	FeS, FeO, Fe_2O_3, Fe_3O_4, $FeSO_4$, $FeCO_3$, $FeCl_2$, $FeCl_3$, $Fe(CO)_5$, $H_2Fe(CO)_4$, $Fe(OH)_2$
21.	Barium:	BaS, BaO, BaO_2, $BaCO_3$, $BaSO_4$, $BaSO_3$, $Ba(NO_3)_2$, $BaCl_2$, $Ba(CN)_2$, BaS_2O_6
22.	Tellurium:	TeS_2, TeO_2, H_6TeO_6, $TeCl_4$, $TeCl_2$, H_2TeO_3
23.	Titanium:	TiO_2, TiH_2, $TiCl_2$, $TiOSO_4$, $Ti(SO_4)_2$, $TiCl_3$, $TiCl_4$
24.	Silicon:	SiO_2, H_2SiO_3, SiC, SiH_4, SiO, SiS_2, $SiCl_4$
25.	Aluminum:	Al_2S_3, $Al_2(SO_4)_3$, $Al_2O_3 \cdot 3SiO_2$, Al_4C_3, $AlCl_3$, AlH_3, AlN, Al_2O_3, $Al(OH)_3$
26.	Magnesium:	MgO, MgO_2, $Mg_2Si_3O_8$, Mg_2Si, $MgSO_4$, $MgSO_3$, $Mg(OH)_2$, MgS_2O_3, $MgCl_2$, $Mg(NH_2)_2$, MgH_2
27.	Calcium:	CaS, CaC_2, $CaCO_3$, $CaCl_2$, CaNCN, $Ca(CN)_2$, CaH_2, CaO, CaO_2, Ca_2SiO_4, $Ca_3Si_2O_7$, $Ca_3Si_3O_9$, $Ca_4(H_2Si_4O_{13})$, $CaSO_4$, CaS_2O_3, $Ca(OH)_2$

MISCELLANEOUS POLLUTANTS

1. Biological Oxygen Demand (BOD)
2. Chemical Oxygen Demand (COD)
3. Thermal Discharge
4. Noise
5. Odor
6. Biological Agents - bacteria, virus, spores, etc.

TECHNICAL REPORT DATA
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16. ABSTRACT: The report gives results of a preliminary evaluation of potential pollutants which could be generated in coal-fired fluidized-bed combustion (FBC) processes. Because SO2 and NOx formation already have received considerable attention from many investigators, the primary emphasis here is on the 'other' pollutants: organic compounds, trace elements, inorganic compounds (other than SO2 and NOx), and particulates. Using available bench scale or pilot plant data and/or simple thermodynamics and empirical correlations with data from other combustion systems, order of magnitude estimates were made of the concentrations of various elements and compounds in the flue gas, in the solid waste, and in the water discharge. Results suggest that, in general, no special environmental problems should result from coal-fired FBC, but that better data are required in several areas, particularly with regard to particle size distributions, possible organic compounds, and the fate of such elements as Be, As, U, Pb, Cd, Ni, Cl, Se, F, and their compounds.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Air Pollution	Flue Gases	Air Pollution Control	13B
Coal	Wastes	Stationary Sources	21D
Combustion	Waste Water	Environmental Assessment	21B, 07C
Fluidized Bed Processing	Organic Compounds	Trace Elements	13H, 07A
Size Screening	Inorganic Compounds	Particulate	07B

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